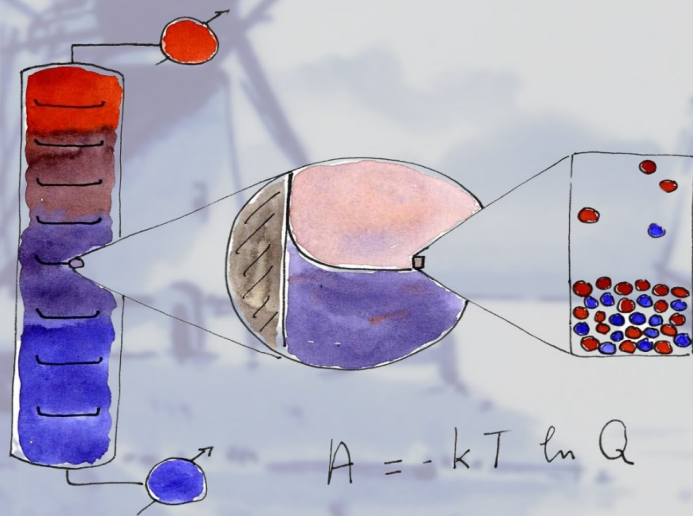


Thermodynamics2024

The 28th Thermodynamics Conference

4-6th September 2024

Book of Abstracts



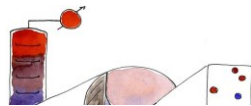
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Program

Day 1

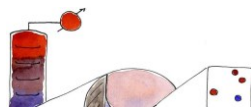
time		Room A
	10.00	Registration (entrance Pathe)
	13.00	Welcome from chair Othon Moulτος
Invited talks (chair: Carmelo Herdes)	13.15	I1.1a Lourdes Vega: Design of catalysts for CO2 conversion and hydrogen production by computational modeling tools
	14.00	I1.2a Andre Bardow: Do Androids Dream of Equations of State?
	14.45	Coffee break (foyer)
Invited talks (chair: Catinca Secuianu)	15.15	I1.3a Erika Eiser: Thermodynamics of Multivalent Nanoparticles in Bacterial Genome Detection
	16.00	I1.4a Antoon ten Kate: Thermochemical perspective on a Transient World (a personal view from an industrial practitioner)
	16.45	Poster session 1 / snacks (foyer) P1.1 - P1.32



Day 2

time		Room A		Room B	
(chair: George Jackson)	9.00	S2.1a Molecular Physics Lecture, Tyler Josephson: Writing Bug-Free Software Using Lean			
	9.45	S2.2a Christopher Wormald Prize lecture, Stefanie Walter: Application of thermodynamic modeling in the design and manufacturing of pharmaceutical formulations			
	10.30	Coffee break (foyer)			
Oral presentations		theme	presentation	theme	presentation
	11.00	CO ₂ and H ₂ (chair: Tim Nijssen)	O2.1a Thijs van Westen: Corresponding-states principle for classical and quantum fluids	Batteries (chair: Sondre Schnell)	O2.1b S. Kjelstrup: The Effect of Ion, Solvent, and Thermal Onsager Coefficients on the Lithium Battery Voltage
	11.15		O2.2a Daniel T. Banuti: Pseudo boiling and molecular network structure in near-critical hydrogen		O2.2b Olav Galteland: Multi-scale modelling of redox-mediated hybrid zinc-air flow batteries
	11.30		O2.3a Catina Secuianu: Are the clathrate hydrates a solution for CCS?		O2.3b Florian Baakes: Assessing Li-ion battery safety: The role of solvents, gas solubility, and salts in pressure evolution
	11.45		O2.4a Felix Llovet: A Consistent Multiscale Simulation for the Characterization of Phosphonium-Based Ionic Liquids in CO2 Capture Applications		O2.4b Henk Huinink: Hydration transitions: water is both reactant and catalyst
	12.00		O2.5a Riccardo Cremona: CO2 capture via solvent-based chemical absorption in an hollow fiber membrane contactor: experimental tests and modelling activities		
	12.15	Machine learning (chair: Frederick de Meyer)	O2.6a Yongchul G. Chung: PACMAN: A Robust Partial Atomic Charge Predictor for Nanoporous Materials Based on Crystal Graph Convolution Networks	Electrolytes (chair: Nefel Novak)	O2.5b Xiaodong Liang: Molecular thermodynamics for water and electrolytes
	12.30		O2.7a Gustavo Chaparro: A continuous machine-learned molecular Equation of State to describe the vapor, liquid, and solid states		O2.6b S. Blázquez: Computation of Electrical Conductivities of Aqueous Electrolyte Solutions: Two Surfaces, One Property
	12.45		O2.8a Thomas Bernet: A machine-learning approach to predict the surface tension of amine-based solvents		O2.7b C. Nieto-Draghi: Critical Micelle Concentration of Perfluoroalkyl Substances in Ionic Aqueous Phase: a combined experimental, Machine Learning and Coarse-Grained molecular simulation study
	13.00		O2.9a Kyrilo Klimentko: ML modeling of acid gases VLE in aqueous MDEA solvents		O2.8b Rasmus Fromsejer: Reliable and fast predictions of the thermochemical properties of solids
				O2.9b Felipe M. Coelho: Thermodiffusion of CO2 in Brine Solutions via Molecular Dynamics Simulations	
	13.00	Lunch break (foyer)			
Invited talks (chair: Gennady Gor)	14.00	I2.1a Randall Snurr: Insights into Capillary Condensation and Hysteresis in Nanoporous Materials from New Simulation Methods			
	14.45	I2.2a Hans Hasse: Machine Learning and Physical Modeling of Thermodynamic Properties of Mixtures			
	15.30	Poster session 2 / coffee break (foyer) P2.1 - P2.32			
	16.30	Free time			
	18.00	Prinsenhof Museum Tour			
	19.30	Conference Dinner at Prinsenhof			

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Day 3

		Room A		Room B	
time		theme	presentation	theme	presentation
Oral presentations	9.00	Porous / confined media (chair: Greg Chung)	03.1a Nickolas Gantzier: Self-diffusion of Volatile Organic Compounds in Zr-MOFs: A Joint Computational and Experimental Study	Aqueous systems (chair: Felix Lovell)	03.1b Callum Donaldson: Green Solutions for Industrial Efficiency: Predicting Cyrene-Water Mixtures for Sustainable Processes
	9.15		03.2a Riya Sharma: Optimizing adsorption refrigeration with MOF-propane integration: a sustainable approach		03.2b Lucia Fernández Sedano: On the possible locus of the liquid-liquid critical point in real water from studies of supercooled water using the TIP4P/ice model
	9.30		03.3a Gennady Gor: Compressibility of Fluids in Nanopores: Molecular Modeling and Ultrasonic Experiments		03.3b Zoe Macpherson: Exploring the Dipole Moment of Supercritical Water and the Hydrogen-Bonding Contributions Involved
	9.45		03.4a Tiong Wei Teh: Effects of mobile framework cations on adsorption in zeolites: GPU-accelerated classical density functional theory		03.4b Willem Gispén: Variational umbrella seeding for calculating nucleation barriers
	10.00		03.5a Thomas Fabiani: Molecular screening of COFs for adsorption of uremic toxins from spent dialysate		03.5b James P.D. O'Connor: Equation of State Informed Potentials: Towards a SAFT- γ -Mie based potential for Mesoscopic Simulation
	10.15		03.6a Samantha Corapi: Understanding the Relationship between Pore Chemical Environment and Hysteresis using a Genetic Algorithm		03.6b Nefeli Novak: Prediction of water anomalous properties by introducing the two-state theory in SAFT
10.30		Coffee break (foyer)			
Oral presentations	11.00	Phase equilibria (chair: Ioannis Economou)	03.7a Cor Peters: Brief Overview of Thermodynamic Achievements in the Period 1970 - 2000 at TU Delft	Thermodynamic modeling at different scales (chair: Mahinder Ramdin)	03.7b Bjørn Hafskjold: Local equilibrium in liquid-phase shock waves?
	11.30		03.8a Happiness Imuetinyan: Phase Behaviour and Density of CO ₂ + Toluene + Cyclohexanol Mixtures at T = 293.15 K to 353.15 K and P = 0.1 to 30 MPa		03.8b Asma Marzouk: Investigation of the Co-TiO ₂ Interaction in Fischer-Tropsch Synthesis through Multi-Scale Simulation Studies
	11.45		03.9a R. Bergmann: Liquid-Liquid Phase Split of Associating Polymer Mixtures		03.9b Jean-Marc Simon: Application of the Kirkwood-Buff solution theory to solid solutions
	12.00		03.10a Riley V. Latcham: Automated Model-Assisted Phase Behaviour Measurements		03.10b Peter Krüger: How to compute density fluctuations at the nanoscale
	12.15		03.11a Saman Naseri Boroujeni: Benchmarking the Predictive Capabilities of the SAFT- γ Mie Eos for Properties of Interest in Pharmaceutical Systems		03.11b Dick Bedeaux: On How to Measure the Subdivision Potential in Nanothermodynamics
	12.30		03.12a Gerard Alonso: On the Compatibility of Butanol + Water + Dimethyl Carbonate blend at its Vapor-Liquid-Liquid Equilibrium		03.12b Jana Zimmermann: Prediction of CO ₂ solubility in semicrystalline polyethylene and the influence of molecular architecture
	12.45		03.13a Wilko Rohfs: ThermoQuiz: Game-based learning of basic thermodynamic principles		03.13b Sondre K. Schnell: Stretching of nucleotide strains in the isometric- and isentensional ensemble
13.00		Lunch break (foyer)			
14.00	S3.1a Lennard-Jones Lecture, Mike Cates: Surprises in the statistical mechanics of active matter (chair: Amparo Galindo)				
14.45	S3.2a Guggenheim Medal lecture, Amparo Galindo: Following Guggenheim: from conformality to molecular modelling and property prediction (chair: Ioannis Economou)				
15.30	Poster award / Conference closure				



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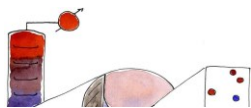
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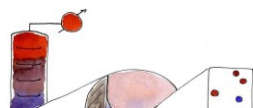
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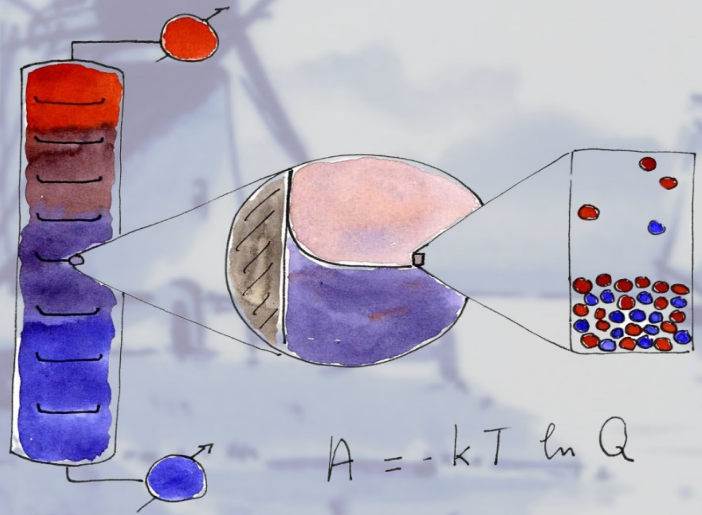
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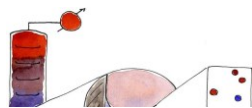
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Special Talks



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S2.1a Writing Bug-Free Software Using Lean

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When developing new methods for molecular simulation, eliminating bugs can be challenging. Programming languages like Python, FORTRAN, and Julia flag syntax errors, but don't (and cannot) catch errors in math or program logic - these must be rooted out by human experts. These issues can be managed by following best practices in software development (such as writing tests alongside the program), but even these do not guarantee that code is correct. Probabilistic programs like Monte Carlo are especially notorious.

Lean is a new programming language whose type system enables it to describe and check the logic of advanced math proofs. By translating derivations in science and engineering into math proofs in Lean, we get a computer-checked proof that the derivations are mathematically and logically correct. We've translated the derivations of Langmuir and BET adsorption theory, as well as proofs about ideal gas thermodynamics and the kinematic equations of motion [1]. We can also write software for scientific computing in Lean, and write proofs about the functions in our execution pipeline, providing guarantees that they have certain properties. Our prototype program performs BET surface area analysis using functions that are logically connected to a formal derivation of BET adsorption theory. We're also building LeanMD, formally-verified molecular dynamics; we'll share our initial work on energy calculations in periodic boundaries. In the future, we aim to logically link LeanMD (and LeanMC!) to formal derivations in classical and statistical mechanics.

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S2.2a Application of thermodynamic modeling in the design and manufacturing of pharmaceutical formulations

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In the early stages of drug development, much about the molecule is still enigmatic, and aspects have yet to be clarified or fully understood. Thermodynamic modeling can allow entering the digital design of drug formulations at an early stage, offering a strategic advantage, filling uncertainties, and enhancing agility and efficiency in advancing the development pipeline. The Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) [1] is used to describe the thermodynamic properties of the involved substances, taking into account the molecular structure and complexities of substances. The presented approach is not limited to a single development phase. It encompasses support in the spectrum from the first to the last stages of drug development, e.g., by thermodynamic modeling of the physical stability (shelf life), the release performance, as well as the manufacturing challenges of the formulation (Figure 1).

For processes like spray drying, understanding the interaction of different solvents with the pharmaceutical formulation is critical. Starting with identifying a homogeneous feed mixture, understanding the solvent drying behavior, finding the process conditions to remove the residual solvents, meeting the regulatory guidelines on residual solvent content in tablets, and reducing toxicity risks can be modeled [2]. For instance, it can be predicted if a mixture might containing faster and slower evaporating components (e.g., acetone and water) would lead to the unwanted accumulation of one solvent in the spray-dried particle within milliseconds, leading to the immiscibility of the formulated components [3]. Immiscibilities can negatively impact the tablet's dissolution performance, which



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can be identified with thermodynamic modeling. The presented approach thus supports identifying the right solvent and process conditions, balancing the solubility of the API and excipients, ensuring regulatory compliance, considering the environmental impact, and minimizing the experimental effort.

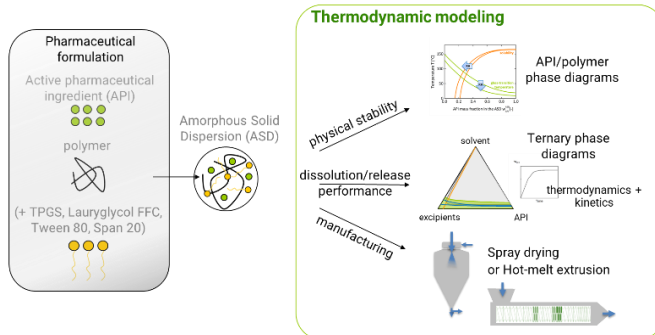
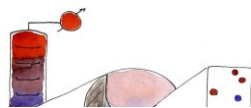


Figure 1: Scheme of thermodynamic modeling fields in drug product development for amorphous solid dispersions.

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S3.1a Surprises in the statistical mechanics of active matter

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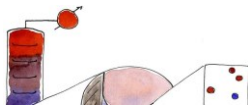
Classical statistical mechanics was invented to describe the macroscopic properties of large numbers of particles. It has a hidden weakness: almost all of its results depend on the microscopic forces being ultimately derived from a Hamiltonian, which governs both the microscopic mechanics and the equilibrium probability distribution (the Boltzmann distribution). This is why quantities like pressure are not only time averages of forces (on a wall), but also thermodynamic state functions (which exist independently of any wall). Active matter systems are different. Their particles take energy out of the environment, and use it for dissipative self-propulsion. Examples include swimming micro-organisms, and synthetic colloids propelled by optical or chemical energy. In such cases the usual connection between interaction forces and thermodynamic behaviour is broken. This leads to some surprising properties, such as the following. (i) The pressure of an active fluid on a wall is not a state function -- it depends on the type of wall. (ii) Random motion in a bath of active particles can be converted into a steady current by introducing inert obstacles, or causing these obstacles to self-assemble by optical modulation of activity. (iii) Fluid-fluid phase separation can arise among active particles in the complete absence of the attractive interactions that cause this in equilibrium. (iv) Various interfacial phenomena, governed in equilibrium by a single surface tension, now depend on several distinct tensions, some of which can be negative.

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S3.2a Following Guggenheim: from conformality to molecular modelling and property prediction

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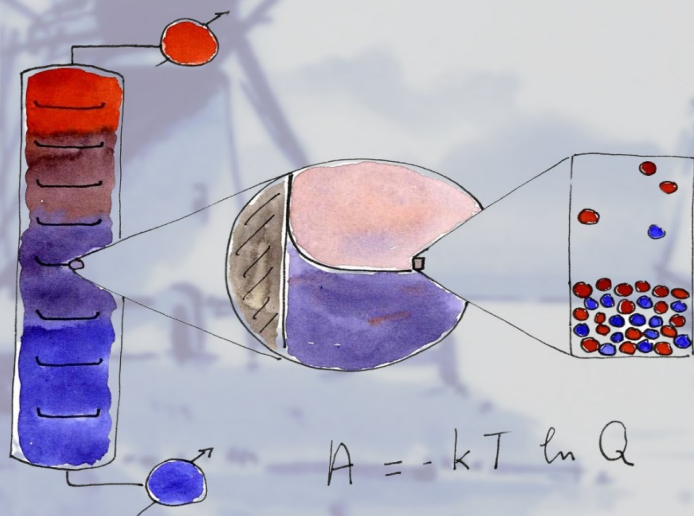
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The fundamental phase diagram of a pure substance exhibiting gas, liquid, and solid phases is reasonably well understood. As the pioneering work of Van der Waals showed, the fluid phase behaviour of simple fluids can be modelled in terms of a balance of spherical repulsive and attractive forces. In the 1940s Guggenheim and others provided experimental evidence that the properties of simple fluids follow a unique master curve when reduced with respect to their critical properties, validating the reduced form of the van der Waals equation. In simple systems, even the fluid-solid transition can be explained in terms of the freezing of a hard-sphere system, although Guggenheim noted early on that the solid phase did not follow the corresponding states principle. A further challenge arises, however, when aiming to model accurately the properties and phase behaviour of mixtures involving complex molecules such as surfactants, polymers, electrolytes, amino acids, or peptides, which are commonly considered in current modelling applications. Modern equations of state, such as SAFT (statistical associating fluid theory), which are based on detailed molecular models have greatly enhanced the capability of analytical methods, and provide a tool that can be used to study complex fluids and their mixtures. I will discuss some of the recent advances in this area; especially the recasting of the free energy expression into a group contribution method, the SAFT- γ Mie equation of state, and the advantage of incorporating a generalised Lennard-Jones Mie potential that leads to a high level of accuracy. The implementation of the Mie potential and the use of a third order expansion in the free energy result in a level of accuracy comparable to that of computer simulations. I will discuss the conformal nature of the Mie potential



in this context. The SAFT- γ Mie group contribution equation of state is especially useful in applications for the prediction of properties of complex fluids in general, and of the solubility of active pharmaceutical ingredients in particular. I will present examples of the predictive ability of the method.

Invited Talks



II.1a Design of catalysts for CO₂ conversion and hydrogen production by computational modeling tools

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Providing sustainable energy to meet the demands for quality of life and economic growth without compromising the environment is one of the greatest challenges we are facing today. Recognizing this need and its urgency some policies have been established, including the Paris Agreement, and strategies have been launched by several countries to reach net-zero emissions by 2050. Among the different technologies, carbon capture, utilization, and storage and low carbon hydrogen have been identified by the International Energy Agency as two key technologies to achieve this goal. Carbon dioxide reduction converting CO₂ into value-added products, by electrochemical or photocatalytic processes is one of the most promising technologies for CO₂ utilization and considerable research and development is devoted in this direction [1]. Furthermore, the use of low carbon hydrogen is expected to significantly increase in the foreseeable future, in line with many countries' efforts to compensate for the declining fossil fuel reserves, together with the search for cleaner sources of energy. Green hydrogen can be produced by water splitting also using electrochemical and photocatalytic processes. The main advantages of photocatalytic processes versus electrochemical processes are that it operates at ambient temperatures and pressures and photocatalyst can be designed with high efficiency and tuning selectivity, making it a promising approach for converting solar energy into chemical fuels.

To develop and select efficient photocatalysts for CO₂ reduction or hydrogen generation (by H₂O or H₂S splitting), it is essential, among other features, to understand the interaction of the molecules with catalysts surfaces, the



mechanism of splitting or conversion, and the limiting barriers; properties that can be provided by quantum methods. After a general introduction, we will showcase the use of DFT for understanding the mechanisms of H_2S adsorption and dissociation on CdS surfaces to produce hydrogen [2], as well as experimental-modeling results on the photocatalytic conversion of gaseous and liquid CO_2 on graphene-impregnated Pt/Cu-TiO₂, discussing the critical role of Cu dopant. Furthermore, we will present some examples of the use of DFT combined machine learning (ML) to guide the selection of efficient photocatalysts for CO_2 reduction and hydrogen generation, focused on a systematic screening of (1) transition-metal-doped Hydroxyapatite for efficient photocatalytic CO_2 reduction [3] and (2) transition metal-doped CdS for photocatalytic hydrogen production [4]. The overall objective is to show how computational modeling tools and ML can help to speed up the development of photocatalytic materials for the desired applications.

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11.2a Do Androids Dream of Equations of State?

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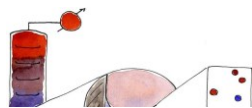
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Thermodynamics is the key to most processes in chemical engineering and has seen substantial advances, allowing us to predict the properties of materials with increasing accuracy. Still, thermodynamics faces significant challenges for humans and molecules: for both students and practitioners, thermodynamics remains an infamous subject. For molecules, available thermodynamic data and methods cover only a tiny part of the basically unlimited molecular space. To overcome both challenges, machine-learning methods [1] have recently been proposed for thermodynamic problems.

In this talk, we will present our recent machine-learning methods for thermodynamics and discuss their potential future role in the engineering toolbox. Our focus will be on a transformer-based model employing the model structure from the well-known ChatGPT model. In particular, we will discuss the SMILES-to-Property Transformer (SPT) which is based on natural language processing to predict thermodynamic properties from SMILES codes of molecules and mixtures [2]. Initially, the SPT model targeted Gibbs excess energy models for activity coefficients.

Beyond G^E -models, SAFT-type equations of state are a promising target for machine-learning methods due to their underlying physical picture, which enhances the meaning of its parameters and supports its use in molecular design. However, the underlying iterative calculations make their use in machine learning challenging. We will present our approach to train the SPT model to predict parameters for the PC-SAFT equation of state [3]. In particular, we will show that thermodynamic insights are essential to arrive at accurate models. The SPT-PCSAFT model accurately predicts complex molecules with various functional groups and even resolves stereoisomers' behavior without special treatments.

This progress allows us to move towards molecular design. Here, we will show how to integrate equations of state models into formulations for computer-aided molecule and process design. These formulations simultaneously optimize molecules with their corresponding process. Thereby, we can automatically identify optimal molecules for applications such as working fluids in power-to-heat processes and solvents and sorbents for CO₂ capture.



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I1.3a Thermodynamics of Multivalent Nanoparticles in Bacterial Genome Detection

Erika Eiser^{1}, Peicheng Xu²*

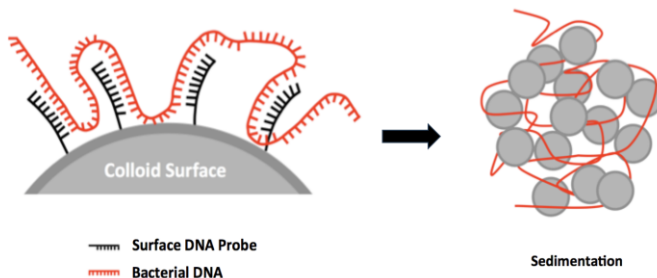
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The thermodynamics of the binding transition of DNA-functionalized colloids is sharp and highly selective [1]. This enables us to drive programmable self-assembly of colloids into designer-made porous systems [2] and various crystals that cannot be achieved with isotropic interactions [3].

Here I will report on such ‘multivalent’ nanocolloids, which are excellent agents to detect whole bacterial genomes. Using the bio-informatics algorithm, developed by Curk et al. [4], we encoded our colloids with maximally multivalent probes that are specific to a given strain of E.coli. With these functionalised colloids we can selectively detect whole bacterial genomes, while reaching sensitivities approaching those achieved with high tech tools such as the PCR (Polymerase Chain Reaction) method [5]. Both the thermodynamic approach and the experiments will be discussed.





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11.4a Thermochemical perspective on a Transient World

A personal view from an industrial practitioner

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We are living in times of strong focus on sustainability and energy transition. The products and services we want as consumers must be produced in more sustainable less energy demanding processes, making use of renewable feedstock, and emitting less waste and reducing the carbon footprint.

There is a multitude of options to improve our footprint on planet earth. But which of the options is most preferred from a sustainable perspective? Thermodynamics is the science relating energy and matter, and as such it is instrumental in process & product design, in the end defining the sustainability profile of the targeted process and product.

Here the author would like to present a personal view on sustainability from a thermochemical perspective. Which routes appear more logical to pursue based on thermochemistry? Can thermochemistry provide an early-stage indication of the impact on sustainability and techno-economics? With this high-level view, the author aims to provide a, hopefully thought provoking, perspective on the role of applied thermodynamics, and therewith perhaps also of its community, in the grand challenges that we are facing.

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12.1a Insights into Capillary Condensation and Hysteresis in Nanoporous Materials from New Simulation Methods

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Capillary condensation and the related phenomenon of adsorption hysteresis can impact applications of porous materials such as gas storage, separations, and adsorption cooling. To better understand these phenomena, we have calculated the adsorption isotherms for methane, ethane, propane, and n-hexane from atomistic grand canonical Monte Carlo (GCMC) simulations in a metal-organic framework having both micropores and mesopores [1]. At low temperatures, the calculated isotherms exhibit sharp steps accompanied by hysteresis. As a complementary simulation method, canonical (NVT) ensemble simulations with Widom test particle insertions are demonstrated to provide additional information about these systems. The NVT+Widom simulations provide the full van der Waals loop associated with the sharp steps and hysteresis, including the locations of the spinodal points and points within the metastable and unstable regions that are inaccessible to GCMC simulations. The simulations provide molecular-level insight into pore filling and equilibria between high- and low-density states within individual pores.

We have also simulated the adsorption and desorption isotherms for argon at 87 K in 1873 MOFs from the CoRE MOF database and for short n-alkanes in selected metal-organic frameworks (MOFs) [2]. Analysis of the molecular configurations showed at least two different mechanisms and origins of hysteresis: one involving a transition in the pores similar to a liquid-to-solid transition and one more similar to a gas-to-liquid transition. The validity of an empirical relationship for the critical pore diameter for hysteresis was also tested using the calculated argon desorption isotherms. The simulations reveal some structures where isotherms exhibit two steps in the adsorption branch and only one step in the desorption branch. Hysteresis loops with a different number of adsorption and desorption steps are quite rare in the literature. To better understand why hysteresis is observed in the GCMC simulations, the concept of the transition probability, which describes the probability of observing a step in the adsorption isotherm at a given pressure in a GCMC simulation, is introduced. We used three different methods to calculate the

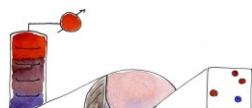


transition probabilities, and we validated that the three methods yielded similar results. The transition probability can be used as a method to quantify and test the convergence of GCMC simulations in the metastable region of an adsorption process.

Focusing on a specific material where GCMC simulations converge very slowly, we used transition matrix Monte Carlo to examine capillary condensation of water in the MOF NU-1000. We found that small changes in the local structure and rotational mobility of hydrophilic sites on the metal nodes of the MOF can have large effects on the macroscopically observed adsorption isotherms.

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I2.2a Machine Learning and Physical Modeling of Thermodynamic Properties of Mixtures

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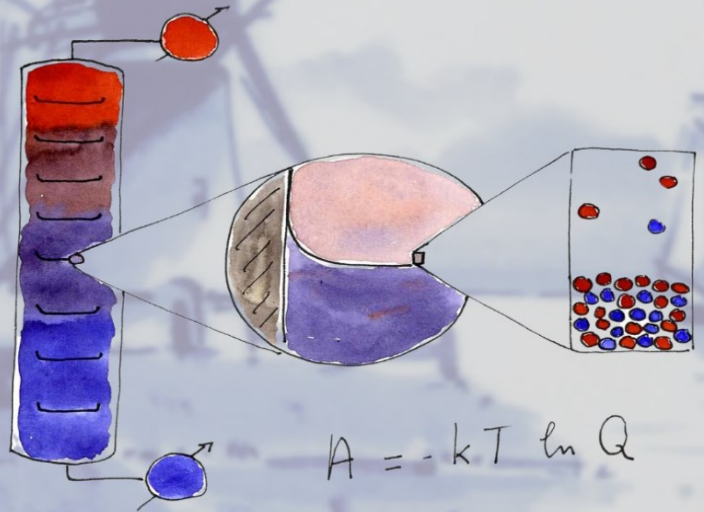
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Information on the thermodynamic properties of mixtures is essential for many tasks in science and engineering. However, since experimental data are notoriously scarce, methods for predicting these properties are needed. Many sophisticated physical methods have been developed for this purpose, approaching the problem in different ways using, for example, equations of state, Gibbs excess energy models, and molecular modeling. Some of these have become standard tools in process engineering. However, predicting properties of mixtures for which no experimental data are available remains a challenge. Recently, new methods from machine learning have been proposed at a remarkable pace to address this challenge. In our presentation, we will compare ML modeling of thermodynamic properties of mixtures with physical modeling, argue that a combination of both approaches is most fruitful, and give examples of the development and application of such hybrid models.



Oral Presentations

Session: CO₂ and H₂



$$A = -kT \ln Q$$



O2.1a Corresponding-states principle for classical and quantum fluids

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We show that quantum-corrected pair potentials, such as the Feynman-Hibbs [1] or Wigner-Kirkwood [2,3] potentials, can be mapped onto classical pair potentials of modified range. A simple mapping based on matching the Van- der-Waals mean-field constants α (integrated dimensionless pair interaction energy) is demonstrated to yield approximately conformal quantum and classical potentials. A quantum-corrected pair potential can thus be described by an effective classical pair potential of equal size parameter σ , well depth ϵ , and mean-field constant α . This establishes a three-parameter corresponding states principle ($\rho^* = \rho\sigma^3$, $T^* = k_B T/\epsilon, \alpha$) that remains applicable in regions of the phase diagram where quantum effects become significant. The accuracy of the principle is verified for thermodynamic properties, vapor-liquid phase behavior, structural properties, and transport properties of Feynman-Hibbs quantum-corrected Mie fluids. Using the corresponding-states principle, we are able correlate and predict thermodynamic properties and vapor-liquid equilibria of hydrogen, deuterium, Helium, and Neon based on an equation of state for classical Mie fluids. Interesting avenues for future research are discussed.

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O2.2a Pseudo boiling and molecular network structure in near-critical hydrogen*Daniel T. Banuti**

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Fluids near the thermodynamic critical point exhibit interesting macroscopic and microscopic properties which have been investigated since their discovery 200 years ago, initially based on the absence of a liquid-gas distinction at high pressures [1]. More recently, it has become clear that distinct liquid(-like) and gas(-like) supercritical states can be distinguished [2]. A transition between the states, pseudo boiling [3], resembles subcritical boiling, and a macroscopic coexistence has been demonstrated under non-equilibrium conditions, such as a temperature gradient [4]. Microscopically, near-critical states are characterized by density fluctuations [5] and non-homogeneities, such as the formation of molecular clusters [6], whose ‘vaporization’ is the microscopic mechanism behind pseudo boiling [7].

The hybrid ergodic lattice gas (HELGa) model, originally demonstrated for argon [8] along the critical isotherm, is now extended to hydrogen. HELGa uses a 3D lattice in combination with analytical equations of state to determine fluid properties as a function of the placement probability P , where a full lattice corresponds to $P = 1$ and $\rho = 3\rho_{cr}$. For low P , HELGa predictively captures average cluster sizes c for a cluster gas model $p_{CG} = 3\rho_{cr}PRT/cM$, see Fig. 1a. For the full P range, the full HELGa model uses the adjacency matrix A of the lattice to account for intermolecular attraction, and the Clausius equation of state for repulsive forces, see Eq. (1), yielding much higher accuracies at high P than Peng-Robinson’s eqn. Figure 1c illustrates how the heat capacity takes the role of a distributed latent heat at the critical point accompanying a drastic step in density, even though macroscopically only one phase is present.

$$p_{\text{HELGa}} = \frac{3\rho_{cr}PRT}{1-P} - \frac{1}{6V} \varpi \|A\|_{\text{sum}} \quad (1)$$

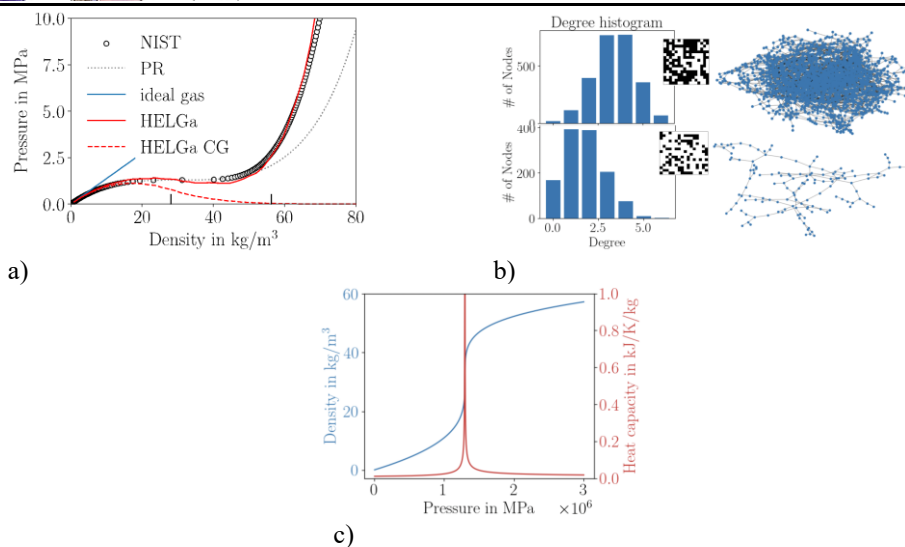
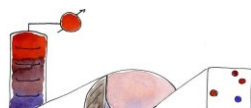


Fig. 1. a): Comparison of HELGa, HELGa cluster gas (CG), Peng-Robinson eqn. (PR), and NIST reference data for hydrogen along the critical isotherm. Black lines at x axis mark $P=0.3$ and $P=0.6$. b): Network analysis of lattice (see inlays) for $P=0.3$ (bottom) and $P=0.6$ (top). Near the critical point ($P=0.33$), the molecules arrange in linear networks; at higher P , the lattice becomes fully connected. c) Illustration of pseudo boiling along critical isotherm. The isobaric specific heat capacity diverges at the critical pressure, taking the role of a latent heat as the density makes a pronounced transition.

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O2.3a Are the clathrate hydrates a solution for CCS?

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Clathrate hydrates have potential applications in various domains (sea water desalination, waste water treatment, natural gas transport and storage, hydrogen storage, materials for the storage of energy and environmental-related gases, gas mixture separation applications, refrigeration and air conditioning applications, photovoltaic applications, exploitation of potential sources of natural gas from permafrost and marine sediments, space, cryo-conservation of biological specimens, etc.) and particularly for carbon dioxide (CO₂) capture, utilisation, and storage (CCUS), where the interest is scientific, technological, and economic [1-2]. As fossil fuels continue to be the major energy supply in the present and near future because of their availability, ease of transport, competitiveness, etc., to meet the CO₂ reduction targets, it is necessary to research and develop a highly effective technology of CO₂ separation and capture (CCS). Gas hydrates (clathrates) are currently getting a significant attention as a potential CO₂ capture technology.

A very recent literature study [3] revealed that in the last years, carbon dioxide captured by using clathrates is increasingly researched. A new installation for investigating the phase behaviour of clathrate hydrates was built, tested, and validated. The main component is a 250 cm³ autoclave, connected with a high-pressure Teledyne Isco syringe pump and a recirculator bath (Julabo) which operates between -50 and 200°C. Phase equilibria of clathrate hydrates of carbon dioxide + different substrates were investigated. The new data were compared with literature ones when available.

Acknowledgment

“This work was supported by a grant from the Ministry of Research, Innovation, and Digitization, CNCS - UEFISCDI, project number PN-III-P4-PCE-2021-0717, within PNCI III”.



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O2.4a A Consistent Multiscale Simulation for the Characterization of Phosphonium-Based Ionic Liquids in CO₂ Capture Applications

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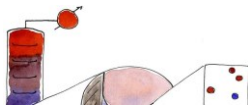
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The development of efficient CO₂ capture systems is essential for managing greenhouse gas emissions. Amines are the most widely used solvents in absorption processes, but they face environmental and economic issues due to evaporation and degradation. Furthermore, there is an urgent need to discover alternative solvents capable of working across a broad range of CO₂ concentrations, from 15% in flue gases to ppm levels in the air. Ionic Liquids (ILs) have emerged as a promising alternative for CO₂ sorbents, thanks to their low vapor pressure and the ability to tailor their solvent power through various ion combinations. Notably, certain phosphonium cation/anion pairings have demonstrated potential in literature, but a comprehensive characterization is necessary to determine the best CO₂ absorber.

This study employs a multiscale approach to investigate CO₂ gas absorption in phosphonium-based ILs with various anions. New molecular models are developed using the soft-SAFT methodology, building on existing soft-SAFT coarse-grain models for this family of ILs [1]. The molecular charge distribution for new ILs is analysed using ORCA and Turbomole software, and association parameters are estimated via DFT calculations. Subsequently, soft-SAFT is used to accurately assess and predict the thermodynamic and absorption properties [2] of these ILs under various conditions. The models account for specific CO₂-IL cross-association interactions to accommodate chemisorption phenomena if present. Additionally, the study considers the presence of hydration. The analysis covers diverse CO₂ compositions and includes estimations of Henry's law constants, solvation enthalpies, and entropies, ultimately identifying the most promising solvents for CO₂ capture.



Acknowledgments

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O2.5a CO₂ capture via solvent-based chemical absorption in an hollow fiber membrane contactor: experimental tests and modelling activities

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This study aims at investigating the potential of hollow fiber membrane contactors as a CO₂ absorption unit through an extensive range of experimental data that will support a detailed process modelling.

The use of hollow fiber membrane contactors (HFMC) in CO₂ capture applications from flue gases is gaining more attention in the gas treatment sector due to their compactness and modularity [1].

The HFMC unit is made up of a series of hollow fibers, with an internal diameter of few microns, encased in a cylindrical cartridge. A microporous polymer based membrane is coated on the external surface of the fiber. The internal packing factor of these modules can reach values higher than 50%. This feature enables to guarantee high interfacial area for mass transfer purposes within a relatively compact unit. In this way, HFMC might be an interesting solutions for those applications in which footprint represent an important limitation (on board ships, etc.).

The CO₂ capture process in an HFMC is the same as the one that occurs in a conventional absorption packed column: the CO₂ is transferred from the flue gases to the liquid solvent due to the interfacial area established between the two phases and thanks to the driving force that is mainly provided by the chemical affinity of the liquid absorbent towards CO₂. From the available literature studies, it is still not clear which is the best flow configuration, whether the solvent should flow in the lumen side (inside the fibers) while the gas in the shell side, or the opposite configuration. Flowing the liquid solvent through the fibers might increase the risk of membrane pores wetting, which is one the major disadvantages of this technology. On the other hand, the gas in the lumen side is subject to higher pressure drops.

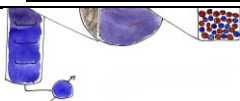


The objective of this work is to characterize from an heat and mass transfer point of view the CO₂ capture process that occurs in the HFMC unit. In this context, a series of laboratory scale experiments have been defined as summarized in Table 1. The liquid solvent to be tested is an aqueous solution of monoethanolamine (MEA) at 30% weight fraction, the benchmark for this kind of processes. Flue gases conditions are reproduced using synthetic mixtures at water saturation conditions. The CO₂ concentration levels (4-20% mol) reflect some typical industrial combustion products. At least two different values of gas flow rate will be set to investigate the effect of gas velocity and fluid dynamics on the membrane contactor performances. Test with and without O₂ in the flue gases are useful to characterize the possible co-absorption of oxygen which can affect solvent degradation. Both flow arrangement with liquid in the lumen and gas in the shell side and vice versa, will be tested in order to establish the optimum flow configuration. Besides the different experimental conditions, it is envisaged also the possibility of testing more than one module in series to increase the available interfacial area and the CO₂ removal rate.

The commercially available 3M™ Liqui-Cel™ EXF-2.5x8 HFMC module will be operated within an experimental set up (Figure 1) which reproduces on a lab-scale the process of absorption/desorption occurring in CO₂ removal plants. With reference to the process scheme of Figure 1, the membrane modules will replace the absorber unit, while the desorption process is performed in the conventional tower.

Table 1. Experimental plan for the CO₂ capture tests with HFMC.

Test #	1) a-b	2) a-b	3) a-b	4) a-b	5) a-b	6) a-b
Gas flow rate, L/h	1000-1500	1000-1500	1000-1500	1000-1500	1000-1500	1000-1500
CO ₂ lean loading (liquid)	0.2 molCO ₂ /molMEA					
L/G ratio (mass)	2 – 5 kg/kg					
N ₂ %mol, dry*	96%	90%	80%	86%	80%	70%
CO ₂ %mol, dry*	4%	10%	20%	4%	10%	20%
O ₂ %mol, dry*	0%	0%	0%	10%	10%	10%
*Water saturated (100% relative humidity)						



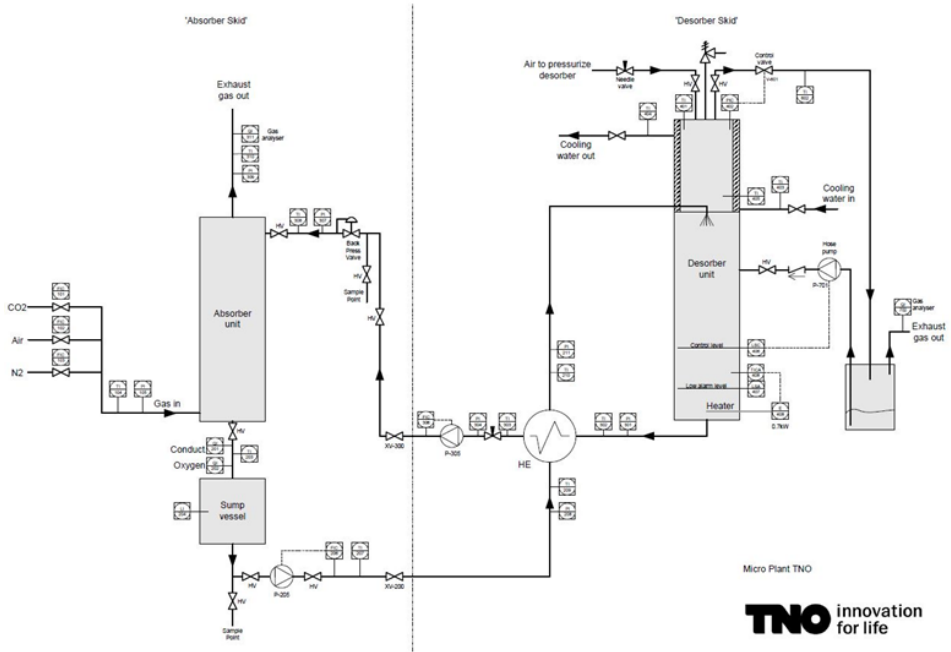


Figure 1. Process flow diagram and instrumentation of the experimental set up.

The outcomes of the experimental tests will be used to validate a numerical model developed for the reactive absorption process of CO₂ into liquid absorbents using membrane contactors. The model is developed according to the rate-based approach and the two film theory [1]. It is a one-dimensional model based on the resistance-in-series method to evaluate the overall mass and heat transfer coefficient in each of the discretization stages along the membrane contactor axial direction. Although it has been developed for CO₂ capture simulations, the model can consider also water vapor and O₂ mass transfer.

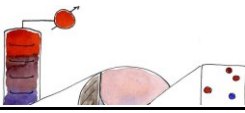
The heat and mass balance equations written along the membrane axial direction and considering CO₂ transfer from the gas to the liquid phase consists of a system of ODEs (Ordinary Differential Equations) reported in equations 1-4:

Gas species mass transfer:

$$\frac{d(Gy_{CO_2})}{dz} = -J_{CO_2}\pi d_{int}n \quad (1)$$

CO₂ loading variation in the liquid phase:

(2)



$$\frac{d\alpha_{CO_2}}{dz} = -\frac{\pi d_{int} n}{LC_{tot,MEA}} J_{CO_2}$$

Energy balance in the gas phase:

$$\frac{dT_G}{dz} = -\left(\frac{n\pi d_{int} q}{GC_p^G}\right) \quad (3)$$

Energy balance in the liquid phase:

$$\frac{dT_L}{dz} = -\frac{n\pi d_{int}}{LC_p^L} \left[q + \left(\sum_i J_i C_{p,i} \right) (T_G - T_{REF}) - J_{CO_2} \Delta H_r - J_{H_2O} \Delta H_{vap} \right] \quad (4)$$

The ODE system corresponds to a boundary value problem that can be solved by defining the inlet composition and temperature of the liquid and gas streams.

The gas species mass transfer flux (J_{CO_2}) is defined in Eq. 5 as the product between the driving force of the absorption process ($(C_{CO_2}^*)_G - (C_{CO_2})_{L,bulk}$) and the overall mass transfer coefficient ($K_{CO_2}^{OV,L}$) estimated with the resistance in series method. In a similar way, the heat transfer flux is given by a global coefficient multiplying the temperature difference between the gas and liquid phase.

$$J_{CO_2} = K_{CO_2}^{OV,L} * [(C_{CO_2}^*)_G - (C_{CO_2})_{L,bulk}]$$

The mass transfer driving force is expressed by the difference between CO_2 concentration in the bulk liquid and the one in equilibrium with the CO_2 partial pressure in the gas. The overall mass transfer coefficient is estimated as an equivalent resistance given by the series of gas, membrane and liquid mass transfer resistance. The experimental results will mostly have an impact on this parameters since their outcomes will be used to calibrate the heat and mass transfer correlations for Sherwood and Nusselt numbers. These dimensionless parameters are used to evaluate the heat and mass transfer resistances in the gas and liquid phases.

The model is developed using Aspen Custom Modeller[®], a tool developed by AspenTech [3] that enables to build customized models for use in the Aspen Plus simulation environment. It is of particularly interest for this application since it provides a well-known thermodynamic framework for the MEA-based CO_2 chemical absorption process. In this way, thermophysical properties such as density and viscosity, and chemical equilibria can be directly retrieved from the software.

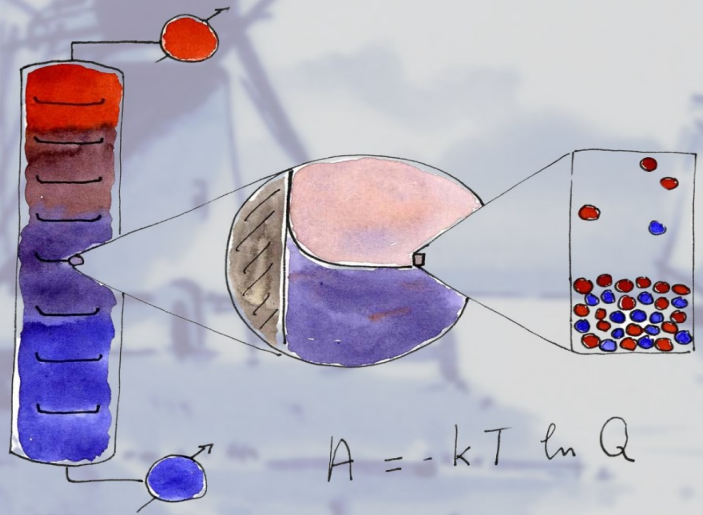


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Oral Presentations

Session: Batteries



$$A = -kT \ln Q$$

O2.1b The Effect of Ion, Solvent, and Thermal Onsager Coefficients on the Lithium Battery Voltage

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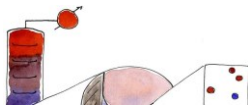
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Understanding and managing polarizations is crucial for optimizing the performance, lifespan, and safety of lithium-ion batteries. We model the lithium-ion battery (LIB) using the theory of non-equilibrium thermodynamics for heterogeneous systems NET [1]. The model is thermodynamically consistent as confirmed with active use of the entropy balance.

We divide the battery into five subsystems: the two bulk electrodes, the two electrode surfaces and the bulk electrolyte. The electrolyte consists of a lithium salt (LiPF₆) and two organic carbonates (DEC and EC). The electrodes are lithium intercalated graphite (anode) and LFP (cathode), what corresponds to a conventional LIB [2]. The work can be seen as an extension of the work of Spitthoff et al. [2], it is a full model using NETH. All transport properties are now available. The electrode surfaces act as a heat source or heat sink, depending on the direction of the electric current flow. As demonstrated by Spitthoff et al. [2], minor changes in one cell can accumulate to a substantial temperature shift when multiple cells are stacked, raising the temperature in the centre by 10 K or more. This finding underscores the importance of understanding and managing temperature variations, especially when dealing with stacked cells. Deviations from a uniform temperature distribution can have significant implications for battery management systems. Steady state solutions for the temperature, concentration and electric potential are presented, using coupling coefficients for electrolyte heat, mass and charge transport in the electrolyte, which recently have become available. The predominant contribution to lost work emanates from the surfaces, associated with the battery voltage drop.

The results provide a more profound understanding of the coupled properties of the cell and has the potential to significantly minimize the overall lost work within the cell.



Acknowledgments

We are grateful to the Research Council of Norway, for the Center of Excellence Funding Scheme, project no 262644, PoreLab.

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O2.2b Multi-scale modelling of redox-mediated hybrid zinc-air flow batteries for more resilient integrated power systems

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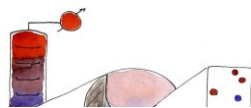
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The proportions of solar and wind in the energy mix are increasing, and the need for energy storage has become apparent [1]. Energy storage, both at the consumer or producer side, is needed to buffer the production and demand peaks. Flow batteries have the potential to provide long-duration energy storage for power grids to handle increased fluctuations in power production [2]. The state-of-the-art stationary batteries, such as vanadium redox flow and lithium-ion batteries, use critical raw materials such as vanadium, lithium and cobalt [3].

Zinc-air redox flow batteries for stationary energy storage is a future technology free of critical raw materials and platinum group metals, resulting in a low-cost energy storage. Zinc and zinc-oxide are abundant materials, and are non-toxic and non-corrosive, and is safer than for example Li-ion batteries (flammable) and H₂ (high pressure and highly flammable) [4, 5, 6]. The challenge with zinc-air redox flow batteries is to confine the zinc in the negolyte tank. If Zn²⁺ is allowed to enter the electrochemical cell, it will form thick layers of zinc metal, drastically increasing the internal resistances, resulting in a poorly performing storage unit with a low round-trip efficiency. We are developing a mediated electrolyte solution, where a mediator carries the electrons for the reduction and oxidization of Zn/ZnO from the negolyte tank to the electrochemical cell. This hinders the deposition of zinc inside the electrochemical cell. However, this raises questions such as the optimal morphology of the Zn/ZnO in the negolyte tank and choice of mediators.

In this work, we are tackling these questions by a multi-scale modelling approach. From molecular dynamics simulations of the mediators to obtain nanoscale transport properties, to pore-network modelling of the negolyte flow in the Zn/ZnO porous structure in the negolyte tank to model flow dynamics on the mesoscale to non-equilibrium thermodynamic continuum modelling of the full redox-flow battery for optimization of energy efficiency.



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O2.3b Assessing Li-ion battery safety: The role of solvents, gas solubility, and salts in pressure evolution

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Next to degradation reactions [1], understanding and controlling pressure evolution during thermal events of Li-ion batteries is a key aspect when assessing the safety of Li-ion batteries [2]. In this study we evaluate the impact of solvent composition, gas solubility, and conductive salts on the pressure built up during exposure of the Li-ion battery to high temperatures (see Figure 1). [3]

We employ a vapour-liquid equilibrium model based on the statistical associating fluid theory (SAFT)- γ Mie equation of state [4], extended to include an ion-pairing model to account for low degrees of salt dissociation in solvents with low dielectric constant, such as linear carbonates. The effect of degradation gases is accounted for by incorporating a CO₂ evolving reaction.

We find that argon or nitrogen are good choices as inert gases during solvent storage and cell assembly, as they only gas out slightly during heating, i.e., they cause negligible pressure increase. Moreover, linear carbonates are found to be preferable over their cyclic counterparts regarding battery safety, as the higher solubility of degradation gases such as CO₂ within them will mitigate pressure evolution during a thermal event. Our study further suggests that the presence of the conductive salt does not substantially affect the pressure evolution. When considering open systems, however, the evaporation of low-boiling linear carbonates will lead to up to a 12% increase in salt dissociation. This should be considered when using open systems, such as online electrochemical mass spectrometry, to obtain reaction parameters.

The insights into the sensitivities of pressure evolution presented here will allow to tailor more precisely the composition of electrolyte mixtures to mitigate safety-critical gas evolution during a thermal event in Li-ion batteries.

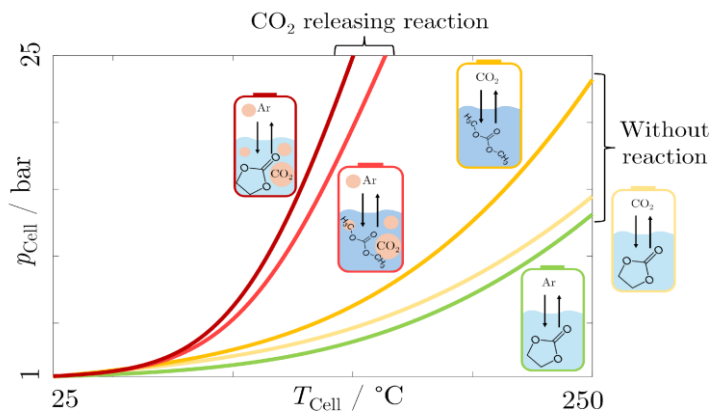
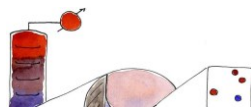


Fig. 1. Graphical summary of the study carried out showing the impact of different pad-gases (Ar and CO₂ are shown here), solvent compositions (e.g. dimethyl carbonate and ethylene carbonate), and of incorporating an evolving CO₂ reaction, on the pressure in a Li-ion cell.

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O2.4b Hydration transitions: water is both reactant and catalyst*Henk Huinink^{1,2*}, Hartmut Fischer³ and Olaf Adan^{1,3}*¹Eindhoven University of Technology,²Eindhoven Institute of Renewable Energy Systems,³TNO

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Salt hydrates are promising materials for making a heat battery. The principle of such a heat battery is based on the reversible hydration reactions that some salts can undergo. During salt hydration, water vapor is absorbed by the salt, while the material undergoes a structural phase transition. At high water vapor pressure, the salt hydrates and at low water vapor pressure the salt dehydrates. The hydration and dehydration reactions are exothermic and endothermic, respectively. The power output is an important property of such a heat battery, which relates to the rate at which water is absorbed/desorbed and the crystalline lattice transforms. Experimentally metastable zones (MSZ) have been observed for many hydration reactions: i.e. zones showing poor kinetics despite the existence of a thermodynamic driving force.

In the past years we have extensively studied hydration processes and the role of metastability. We have shown that two factors determine the size of this metastable zone. First, in the MSZ a nucleation barrier exists leading to large induction times for the reaction [1]. We have successfully applied classical nucleation theory (CNT) to explain the relation between the induction time for nucleation and the water vapor pressure. The second factor at play is related to the dynamics of ions on small scales. The rate at which a crystalline lattice of a salt can remodel is related with the mobility of ions. We have found that ionic mobility at interfaces play a key role [2]. With increasing water vapor pressure, more water adsorbs to the interfaces, which facilitates local dissolution of ions. So, the water vapor pressure not only determines the driving force of the hydration reaction, but also facilitates the reaction by accelerating the ionic mobility.

Due to these findings, we could identify suitable dopants that boost hydration kinetics and therefore the power output of salt-based heat batteries [3][4]. Small amounts of extreme deliquescent ionic compounds locally attract water and increase the ionic mobility.



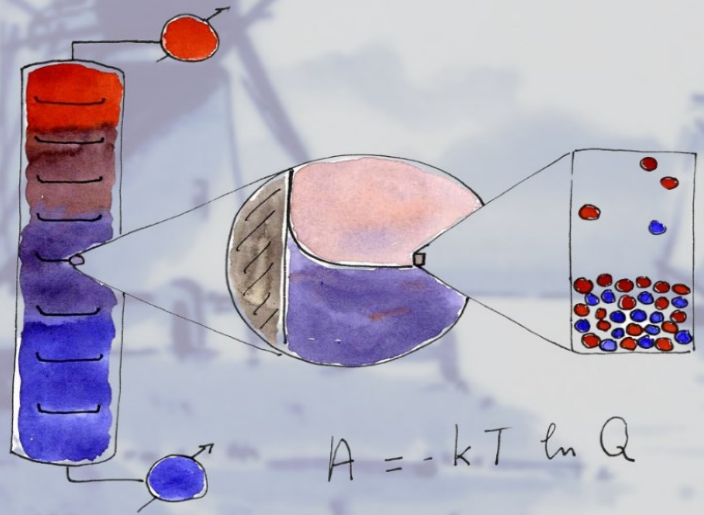
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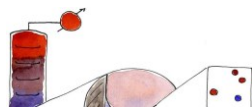


Oral Presentations

Session: Machine learning



$$A = -kT \ln Q$$



O2.6a PACMAN: A Robust Partial Atomic Charge Predictor for Nanoporous Materials Based on Crystal Graph Convolution Networks

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We report a fast and easy method (PACMAN) to assign partial atomic charges on metal-organic framework (MOF) and covalent-organic framework (COF) crystal structures based on graph convolution networks (GCN) trained on >1.8 million high-fidelity partial atomic charge data obtained from the Quantum Metal-Organic Framework (QMOF) database. The developed model shows outstanding performance, achieving a mean absolute error (MAE) of 0.0055 e in test set while maintaining consistency with DDEC6, Bader, CM5 and REPEAT charges across diverse chemistry and topologies of MOFs and COFs. We find that the new method accurately assigns partial atomic charges for ion-containing nanoporous materials, which has not been possible in previous machine learning (ML) models. Grand canonical Monte Carlo (GCMC) simulation results for CO₂ and N₂ uptakes and the Widom particle insertion calculation for Henry's law constant of H₂O results based on PACMAN and the original DDEC6 charges show excellent agreements. The runtime analysis of the new method demonstrates that the partial atomic charges of MOF and COF structures with up to 500 atoms can be obtained in less than 10 s. An easy-to-use web interface has been developed to facilitate the adoption of the developed model.



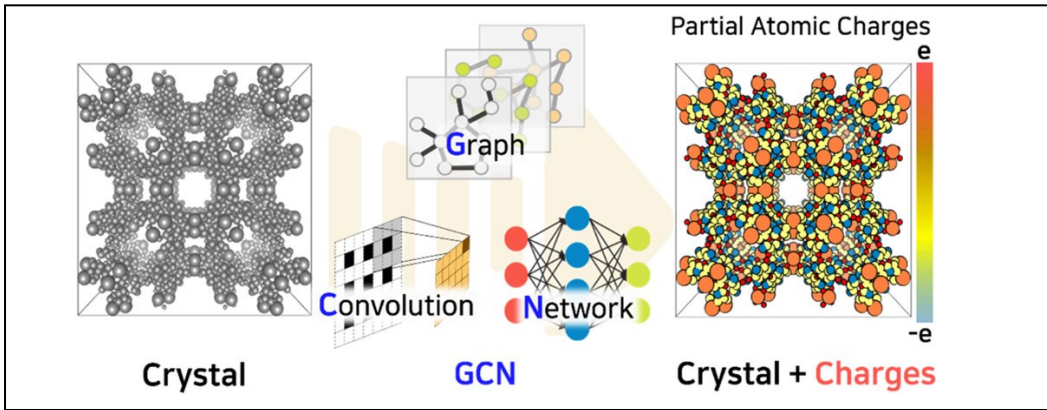
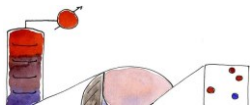


Fig. 1. The workflow of PACMAN charges program.

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O2.7a A continuous machine-learned molecular Equation of State to describe the vapor, liquid, and solid states

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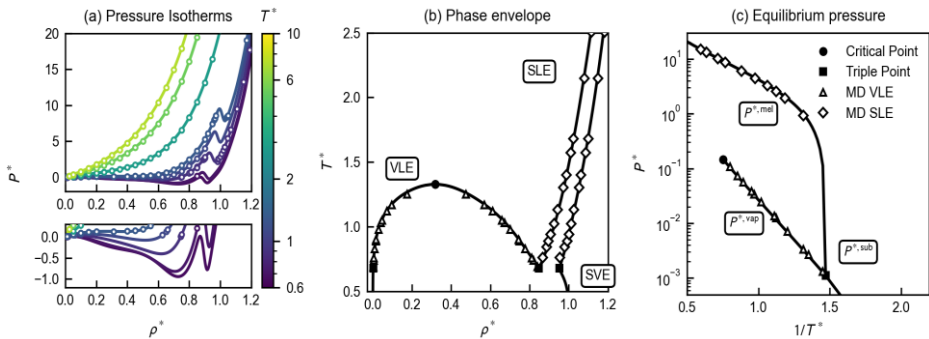
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In 1874, J.C. Maxwell [1] developed a thermodynamic surface model that displayed how the different aggregation states of matter (fluid and solid) could potentially be mapped into a single mathematical function. This idea partially inspired J. D. van der Waals [2] to develop his Equation of State (EoS), which can continuously model the thermophysical properties of both the gas and liquid states. EoSs of this family exhibit a so-called “van der Waals loop”, i.e. the maximum and minimum pressure defining the regions of instability and meta-stability between fluid phases. Surprisingly, analogous approaches have not been popular when considering the solid-fluid equilibrium and instead, the field employs discontinuous models where independent and functionally distinct EoS represent the fluid and solid states. Based on Maxwell’s premise, we employ a single EoS framework to simultaneously model fluid and solid phases. We employ an artificial neural network to continuously quantify the thermophysical properties of a molecular model from the ideal gas up to the crystal phase. This Free Energy – Artificial Neural Network (FE-ANN) EoS is showcased here for the Mie particle [3].

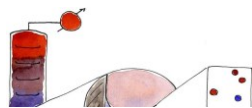
The FE-ANN(s) EoS is trained using 1st and 2nd-order thermophysical properties obtained from molecular simulation and accurately models seen and unseen properties. Because of its physics-informed formulation, the FE-ANN(s) EoS can predict thermophysical properties for which it was not trained. Although fitted to single-phase data only, the FE-ANN(s) EoS “discovers” the unstable van der Waals loops that can predict Vapor-Liquid Equilibria (VLE), Solid-Liquid Equilibria (SLE) and Solid-Vapor Equilibria (SVE). Moreover, the FE-ANN(s) EoS predicts the triple point. As an example, pressure isotherms and the phase diagram of the Lennard-Jones fluid are shown in Figure 1.





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O2.8a A machine-learning approach to predict the surface tension of amine-based solvents

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Carbon Capture and Storage [1] is a promising technology to reduce carbon dioxide (CO₂) emissions. Industrially, the most common solvents used currently are amine-based solvents as they have good reactivity to absorb CO₂ from flue gases and can then be regenerated to release and store the captured CO₂. The knowledge of the thermodynamic and kinetic properties of amines and their mixtures, is crucial for optimizing the process; furthermore, stream viscosity and surface tension enable equipment sizing [2].

We develop a machine-learning (ML) approach to predict the surface tension of amine-based solvents. The approach is combined with a group-contribution method that makes surface tension prediction possible for new solvents that incorporate single amines as well as blends. We assess the accuracy and reliability of our ML model, and we perform comparisons with standard methods, e.g., empirical equations and molecular-based models. Moreover, considering our choice for a group-contribution ML model, we establish a connection with the SAFT- γ Mie groups [3] that can be used in computer-aided design frameworks to optimize CO₂ capture processes.

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O2.9a ML modeling of acid gases VLE in aqueous MDEA solvents

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Methane sourced from natural reservoirs contains admixtures of acidic gases, such as H₂S and CO₂, which exhibit corrosive properties and degrade the fuel quality of methane. The conventional method for removing these acidic gases involves their absorption and subsequent reaction with aqueous alkanolamine solutions. Methyldiethanolamine (MDEA) has emerged as a popular alkanolamine due to its favorable attributes, including selectivity towards H₂S, low heat of absorption, and reduced corrosiveness.

An essential metric reflecting the efficiency of absorbents is the Vapor-Liquid Equilibria (VLE) curves depicting the relationship between acid gases and the absorbent. These curves illustrate the extent to which the alkanolamine binds the gas compared to the remaining gas phase quantity. Measuring VLE concentrations is a time-intensive endeavor necessitating numerous repetitions for various combinations of temperature and MDEA concentration in H₂O. Theoretical models (e.g. e-NRTL) for VLE prediction in a ternary system (e.g. CO₂-H₂O-MDEA) require experimental VLE and other thermodynamic data on all binary systems and on the ternary system.

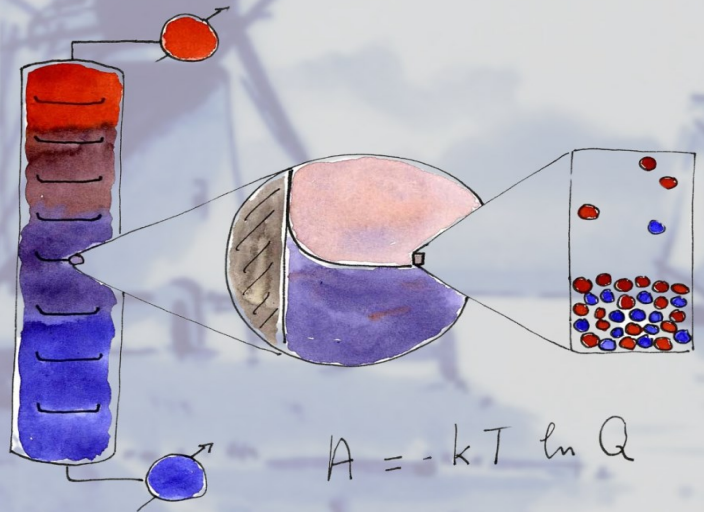
As a solution to this resource-intensive process, machine learning (ML) modeling has been employed to predict gas vapor pressure based on its concentration in the absorbent, temperature, and MDEA concentration in H₂O. Data was collected from 15 articles, resulting in 512 data points (61 isotherms) for CO₂-MDEA-H₂O and 239 datapoints (34 isotherms) for H₂S-MDEA-H₂O. Data analysis techniques were applied to the available data, and the resulting models were evaluated for their robustness and predictive capability. The prediction error was deemed acceptable, and the shapes of the experimental VLE curves were



generally preserved. Additionally, the predicted curves in the absence of experimental data were consistent with lower temperatures corresponding to higher absorption capacity.

Oral Presentations

Session: Electrolytes



$$A = -kT \ln Q$$

O2.5b Molecular thermodynamics for water and electrolytes

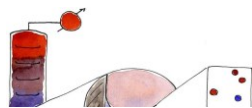
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Apart from experimental data, thermodynamic models and theories stand as essential tools for diverse industrial applications, providing the scientific foundation for process and product development, design, and optimization, as well as environmental impact minimization, safety assessment, and the creation of digital twins of manufacturing assets in the new era.¹⁻³ They have undergone a remarkable evolution since the pioneering van der Waals equation of state, with Statistical Associating Fluid Theory (SAFT) models now recognized as the most sophisticated tools for investigating phase equilibria and various physical properties of hydrogen-bonded mixtures. Despite significant advancements over the past decades, thermodynamic models and theories continue to face numerous challenges, particularly when dealing with water and electrolytes.^{1,2}

Water exhibits exceptional behaviors that deviate significantly from typical liquid ones. These deviations, commonly referred to as 'water anomalies', include its unusual density maximum at 4°C under atmospheric pressure, which vanishes at high pressures and shifts to lower temperatures with the addition of electrolytes. These anomalous properties have wide-ranging implications for various fields of human interest and have been a subject of intense scientific inquiry for centuries. While state-of-the-art thermodynamic models can adequately describe the phase equilibria and some physical properties of many water-containing systems, they fall short in capturing the full spectrum of water anomalies. Electrolyte systems play pivotal roles in diverse applications such as carbon capture and sequestration, acid gas removal, desalination, sour water stripping, solution mining, ocean acidification, energy storage, heavy metal pollution, lithium refining, bioinorganic understanding, and more. This vast array of systems presents one of the most formidable engineering challenges for thermodynamic models and theories. This presentation will discuss the capabilities and limitations of the current state-of-the-art models and theories for water and electrolytes, and we will also discuss whether a 'two-state' concept can provide a better framework for these systems.



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O2.6b Computation of Electrical Conductivities of Aqueous Electrolyte Solutions: Two Surfaces, One Property

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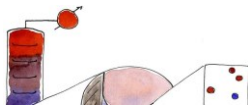
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In this work, we computed electrical conductivities under ambient conditions of aqueous NaCl and KCl solutions by using the Einstein–Helfand equation [1]. Common force fields (charge $q=\pm 1e$) do not reproduce the experimental values of electrical conductivities, viscosities, and diffusion coefficients [2]. Recently, we proposed the idea of using different charges to describe the potential energy surface (PES) and the dipole moment surface (DMS) [3]. In this work, we implement this concept. The equilibrium trajectories required to evaluate electrical conductivities (within linear response theory) were obtained by using scaled charges (with the value $q=\pm 0.75e$) to describe the PES. The potential parameters were those of the Madrid-Transport force field [4], which accurately describe viscosities and diffusion coefficients of these ionic solutions. However, integer charges were used to compute the conductivities (thus describing the DMS). The basic idea is that although the scaled charge describes the ion–water interaction better, the integer charge reflects the value of the charge that is transported due to the electric field. The agreement obtained with experiments is excellent, as for the first time electrical conductivities (and the other transport properties) of NaCl and KCl electrolyte solutions are described with high accuracy for the whole concentration range up to their solubility limit [5]. Finally, we propose an easy way to obtain a rough estimate of the actual electrical conductivity of the potential model under consideration using the approximate Nernst–Einstein equation, which neglects correlations between different ions.



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O2.7b Critical Micelle Concentration of Perfluoroalkyl Substances in Ionic Aqueous Phase: a combined experimental, Machine Learning and Coarse-Grained molecular simulation study

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PFAS (per- and polyfluoroalkyl substances) is a category of molecules that includes a wide variety of chemical functional groups such as alcohols, ethers, esters, and surfactants, all featuring a fully or partially fluorinated carbon chain. These compounds are found in numerous products and chemicals, including pesticides, plastics, cosmetics, and food packaging [1]. However, the exceptional advantages of PFAS come with significant drawbacks. They are resistant to degradation and persist in the environment, earning them the labels "eternal pollutants" or "forever chemicals" [2]. Even at low doses, PFAS are suspected of interfering with the hormonal system. At the European and international levels, some PFAS have already been restricted or even banned [3]. Nevertheless, most of these substances remains unregulated and are still authorized for use. Despite the PFAS family encompassing thousands of compounds, only a small number have been experimentally characterized, and the available data in the literature remains limited.

The development of robust predictive models to address this lack of information is of the utmost importance. In response to this need, our work presents numerical models that describe the behavior of these persistent chemicals in aqueous environments. PFAS compounds are surfactants with a hydrophilic head and a tail being both hydrophobic and lipophobic (see Figure 1.a). It has been hypothesized that the capacity of PFAS surfactants to form micelles may influence their adsorption or solubility-related properties. In this context, the critical micelle concentration (CMC) is a key factor for understanding their behavior in the environment and is crucial for developing capture or purification processes. To obtain reference CMC values for PFAS and alkyl sulfates, we conducted a

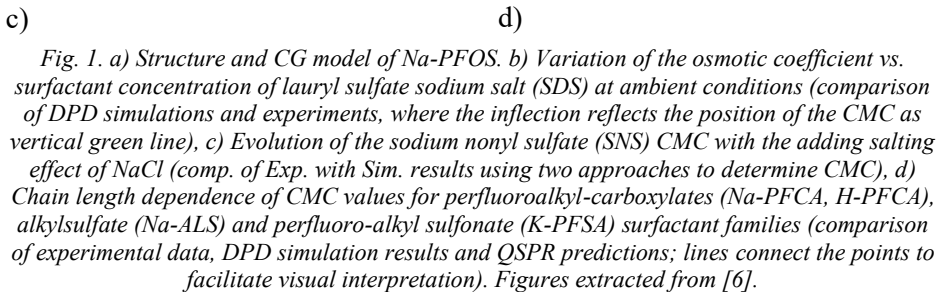


comprehensive literature review to identify reliable experimental CMC values. These values were used as fitting targets for the simulation method developed in this work as well as to train a quantitative structure-property relationship (QSPR) model for comparative purposes [4].

Our approach accurately reproduces surfactant aggregation behavior under various conditions, including ionic strength. We have developed a robust parameterization methodology, incorporating a recent relationship involving hydration free energy values from Density Functional Theory (DFT) [5], to create Coarse-Grained (CG) models for PFAS using the Dissipative Particle Dynamics (DPD) approach. This strategy relies on matching the CMC values obtained by observing the inflection point in the osmotic pressure/coefficient as a function of surfactant concentration (see Figure 1.b). The models have been tested by reproducing our experimental results on the variation of the CMC at different salinities (see Figure 1.c). The successful modelling of the CMC ensures that the methodology accurately parameterizes the species under different conditions. This methodology allows for precise prediction of CMC values for a diverse range of surfactants, including those based on hydrocarbons and PFAS (see Figure 1.d) [6].

We anticipate that these models can be reliably employed to predict the interactions of other PFAS substances with greater structural and chemical complexity. The models can also forecast other important environmental properties, including partition coefficients and contaminant adsorption, while accurately considering the realistic salinity found in natural waters.





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O2.8b Reliable and fast predictions of the thermochemical properties of solids

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Many applications involving salts in medicine, energy storage, geology and materials science involve solid-liquid equilibria. However, there are currently no models to predict the precipitation of these salts without experimental data. This limitation severely impacts e.g. the predictive power of electrolyte models applied to systems involving solids, especially when experimental data for the solids are scarce.

To overcome this challenge we have combined quantum chemistry, machine learning, experimental data and statistical data analysis [1]. The result is a robust and highly predictive approach, which provides accurate predictions of the thermodynamic properties of solids in a rapid manner. These properties are able to be readily integrated into datasets for use in e.g. electrolyte modelling, materials science etc..

I will present our work on a framework within the reaction network approach which enables accurate and efficient high-throughput prediction of various thermodynamic properties of solids utilizing both atomistic and electronic models.

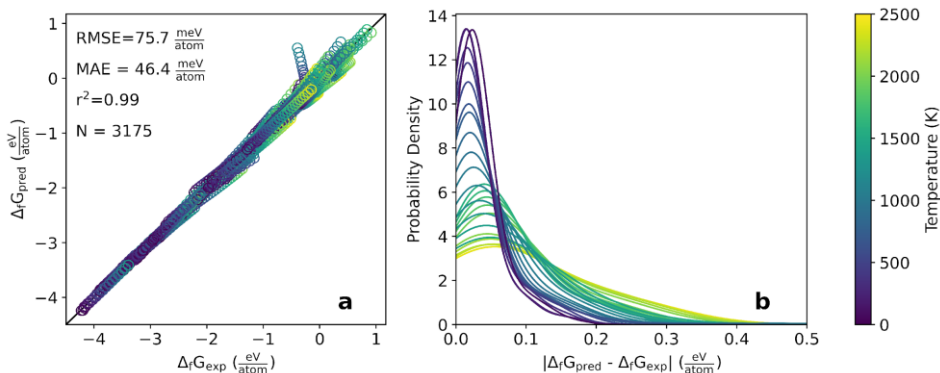
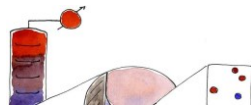


Fig. 1. Benchmarking Gibbs free energy of formation predictions from 0-2500 K for 230 compounds. (a) Parity plot of predicted Gibbs energies of formation against experimental data. (b) Probability density distribution of absolute errors of predicted Gibbs free energies at the different temperatures. RMSE is root mean squared error, MAE is mean absolute error, r^2 is the correlation coefficient and N is the total number of data-points.

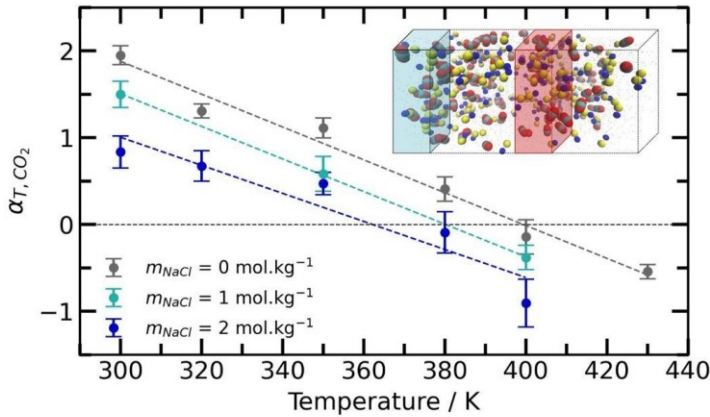
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O2.9b Thermodiffusion of CO₂ in Brine Solutions via Molecular Dynamics Simulations*Felipe M. Coelho*¹, Luís F. M. Franco^{1*}, Abbas Firoozabadi²¹ Universidade Estadual de Campinas (Unicamp), Campinas, SP, Brazil,²Reservoir Engineering Research Institute (RERI), Palo Alto, CA, USA

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Some formations aimed for geothermal energy harvesting or carbon long-term storage (deep saline aquifers) may contain a very high vertical temperature gradient. The components of a fluid mixture may segregate due to the thermodiffusion, also known as Soret effect, a coupling phenomenon in which mass flux can be induced by a thermal gradient, establishing a concentration gradient in the steady state. In our work, we evaluate the CO₂ thermodiffusion in brine mixtures via molecular dynamics (MD) simulations to understand how the geothermal gradient may affect CO₂ vertical distribution within subsurface formations. We propose a framework to evaluate the thermal diffusion factor in multicomponent mixtures accounting for cross-diffusion effects. When the mixture contains more than two components, the thermal diffusion is no longer dependent only on the thermal segregation, but also depends on the mass diffusion coefficient. From non-equilibrium MD, we evaluate the segregation of the components with temperature using the eHeX method, and from equilibrium MD we compute the Fickian diffusion matrix based on the Onsager coefficients and the thermodynamic factors. The force field choice is validated against experimental data of brine thermodiffusion and CO₂ diffusion in water and NaCl brine. The thermodynamic factor matrix from MD shows good agreement with the one computed using

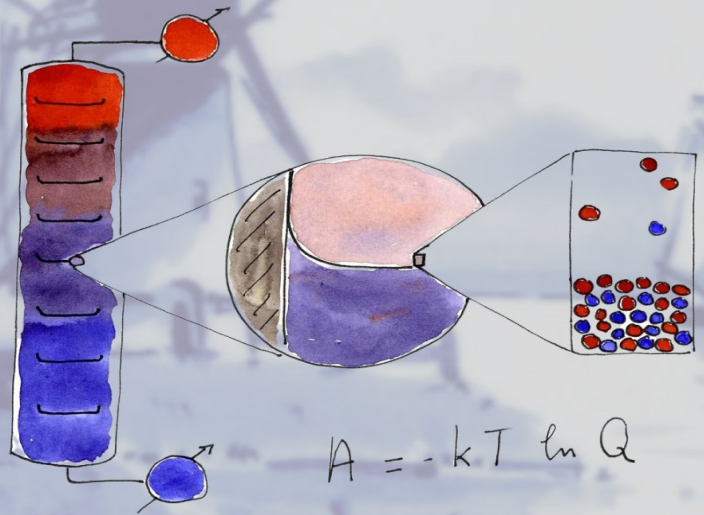


the e-CPA equation of state. The CO_2 Soret effect has a pronounced dependence on temperature and salinity. By increasing temperature or salinity, CO_2 migrates from thermophobic to thermophilic. Comparing the molecular structures in the thermodiffusion inversion point, we find very similar water-water radial distribution functions, which indicates that water structure may have a dominant effect on the CO_2 Soret effect. The more organized the hydrogen bond network (lower temperature or salinity), the more thermophobic is CO_2 . We also investigate different types of alkali metal brines, namely KCl and LiCl. The temperature dependency and the hydrogen bond network are about the same independent of the type of brine. Our results and formulation advance the knowledge of CO_2 distribution in subsurface formations by providing a way to account for thermodiffusion in the compositional grading of formations aimed for carbon sequestration and heat extraction.



Oral Presentations

Session: Porous/ confined media



$$A = -kT \ln Q$$



O3.1a Self-diffusion of Volatile Organic Compounds in Zr-MOFs: A Joint Computational and Experimental Study

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The association of specific volatile organic compounds (VOCs) in exhaled human breath (EHB), often called a chemical “fingerprint”, to a particular disease is a growing field of study. The ability of trained scent dogs to identify COVID-positive respiratory secretion samples lends itself to the possibility of developing a non-invasive, breath-based diagnostic tool to provide insight into a person’s state of health. However, detecting the target constituents --- often existing at dilute concentrations in a complex mixture of water, CO₂, and other VOC interferents -- poses a significant challenge.

Metal-organic frameworks (MOFs) have demonstrated tremendous aptitude for applications in gas sensing and separation technologies. MOFs are porous, crystalline solids composed of metal nodes coordinated by organic linkers which form an extended network. Zirconium (Zr) MOFs exhibit exceptional thermal and hydrolytic stability which makes them attractive candidates for studying VOC detection in EHB. If MOFs are to be used in a breath-based diagnostic tool, understanding the interactions between the VOCs and the MOF is vital.

In this work, we use molecular dynamics simulations and experimental NMR to study the self-diffusion properties of several polar and non-polar VOCs in a topologically diverse set of Zr-MOFs. We compute self-diffusion coefficients at multiple loadings over a range of temperatures and compare against experimental values. We will discuss trends between self-diffusion and heat of adsorption, molecular properties (e.g. chain length, polar or non-polar, and isomers), and framework topology. Finally, we consider the challenges of comparing simulation to NMR experiments.

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O3.2a CoRE MOF Screening for Optimal Propane Adsorption Refrigeration

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The adsorption refrigeration cycle (ARC) is a sustainable refrigeration process that fundamentally replaces the energy-intensive compressors in a vapor compression cycle (VCC) with an adsorbent bed that uses solar energy or waste heat for regeneration. This has been experimentally shown to be a sustainable alternative to the VCC cycles. Metal-organic frameworks (MOFs) have been proven to be excellent adsorbents compared to the traditionally used zeolites, silica gel, and activated carbon owing to their ordered structure and tunable characteristics. In this study, we explored the integration of MOFs with a proposed low-global warming potential (GWP) refrigerant, propane. Using propane as the refrigerant fluid, we performed a computational screening on the CoRE MOF database to identify the optimal MOFs for use as an adsorbent in this application. We discovered a maximum coefficient of performance (COP) for refrigeration of approximately 0.6, which is significantly higher than those obtained using widely used adsorbents like zeolites, silica gel, and activated carbon. We also investigated the cooling capacity (CC) of the MOF-propane pair and obtained a remarkable CC of around 95 kJ/mol. An insight into the structural characteristics of MOF that influence the COP and CC has also been studied. A further 17% increase in the COP is achieved with an optimization of the conditions. This work offers fundamental insights into choosing MOFs as adsorbents in ARC, which can in the future be explored to make the refrigeration process more sustainable.^{1,2}

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O3.3a Compressibility of Fluids in Nanopores: Molecular Modeling and Ultrasonic Experiments

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Fluids confined in nanopores are ubiquitous in nature and technology. In recent years, the interest in confined fluids has grown, driven by research on unconventional hydrocarbon resources – shale gas and shale oil, much of which are confined in nanopores. When fluids are confined in nanopores, many of their properties differ from those of the same fluid in the bulk. These properties include density, freezing point, transport coefficients, thermal expansion coefficient, and, as it was shown recently, compressibility [1].

The compressibility of a fluid confined in the pores contribute to the overall elasticity of the fluid-saturated porous medium and determine the speed at which elastic waves traverse through the medium. In this talk I will show how compressibility of a confined fluid in a nanopore can be calculated based on Monte Carlo, and molecular dynamics simulations [2], and illustrate it with calculations for various fluids. Additionally, I will present our recent experimental measurements of elastic properties of water confined in nanoporous glass samples [3]. Our results suggest that some of the models widely used for describing elasticity of fluid-saturated porous solids need to be revised.

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O3.4a Effects of mobile framework cations on adsorption in zeolites: GPU-accelerated classical density functional theory

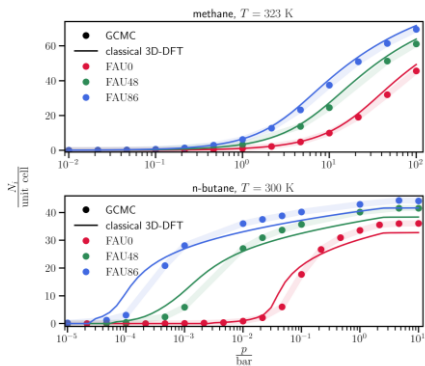
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In this study, we utilize Grand Canonical Monte Carlo (GCMC) simulations and three-dimensional classical density functional theory (3D-cDFT) employing the perturbed-chain statistical associating fluid theory (PC-SAFT) to predict the adsorption properties of zeolites. Building upon previous work that demonstrated good agreement between GCMC and 3D-cDFT for light gases in covalent organic frameworks (COFs) [1], we extend our investigations to zeolites containing mobile cations. Framework cations influences the adsorption isotherm [2]. Our approach incorporates mobile cations into DFT by fixing cation positions within the framework in their energy-minimized state. A recent implementation of 3D-cDFT which leveraged parallelized reverse-mode automatic differentiation on GPU significantly speeds up computational time when compared to FeOs [3]. This significant speedup enables high-throughput screening of adsorbents. 3D-cDFT also enables simultaneous process and topology optimization by providing noise-free adsorption isotherms curves. The ability to capture the effects of framework cations in adsorption isotherms in 3D-cDFT opens avenues for broader applications in material design and adsorption property predictions. The figure below shows the adsorption isotherms of methane and n-butane in faujasites (left), a subclass of zeolites, computed using GCMC and 3D-cDFT as well as the comparison of computational times (right). The X in FAUX represents the number of sodium framework cations per unit cell.





System	t_{comp}	FeO ₂	JAX	Speedup
FAU0 methane	t_{min}/s	12.15	0.576	21
	t_{max}/s	188.6	5.885	32
	$t_{\text{all}}/\text{min}$	39.50	1.112	35
FAU86 methane	t_{min}/s	59.40	1.579	38
	t_{max}/s	272.0	6.974	39
	$t_{\text{all}}/\text{min}$	56.00	1.464	38
FAU0 n-butane	t_{min}/s	0.743	0.022	34
	t_{max}/s	578.0	11.43	51
	$t_{\text{all}}/\text{min}$	96.87	2.017	48
FAU86 n-butane	t_{min}/s	0.745	0.023	33
	t_{max}/s	477.2	10.80	44
	$t_{\text{all}}/\text{min}$	158.1	3.882	41

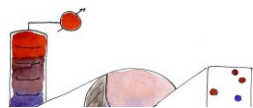
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$A = -kT \ln Q$



O3.5a Molecular screening of COFs for adsorption of uremic toxins from spent dialysate

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Hemodialysis (HD) is the life-supporting treatment for 2.6 million patients with end stage kidney failure, affecting 9.7 million people worldwide. HD replaces kidney functionality, clearing uremic toxins (UT) from blood. The technology is based on the exchange of UTs through a semipermeable membrane with a buffered solution, called dialysate. The lack of access to affordable treatment resulted in 1.2 million deaths in 2017. The treatment is discontinuous, delivered in 2-3 sessions per week, in hospital. This has a detrimental impact on the patient lifestyle and it results in vascular stress, accumulation of UTs and post-treatment hangover. Almost 120L of dialysate are required for each session. The water consumption represents the bottleneck to design a wearable artificial kidney (WAK), which would boost accessibility of hemodialysis, improving life expectancy and lifestyle of patients.

Current technology for WAKs involves enzymatic or electrochemical conversion of urea, that is the most abundant and hard-to-remove compound, but issues for patient's safety has been raised. Conversely, a technology involving a capture mechanism of UTs is intrinsically safe. The fabrication of a mixed matrix membrane, a composite material formed by adsorbing particles onto a porous polymeric support, revealed to guarantee optimal fluid dynamic condition and low energy consumption [1], [2]. Nonetheless, conventional adsorbers used so far showed to be poorly effective in capturing urea. Moreover, discovery and screening of new materials are strongly empirical and based on trial and error. Organic Frameworks (MOFs and COFs) are a class of frameworks that gained interest in water remediation, but their potential toward UTs still need to be thoroughly investigated.

COFs are synthesized by organic building units, which assemble to form periodic and highly porous frameworks. The combination of a high number of units available gives the chance to tailor stable organic crystals, with tunable porosity in terms of size and chemical environment. Furthermore, they offer higher stability in



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moist conditions and in acidic or basic environment. However, COFs have been scarcely studied for water and UTs sorption using molecular simulations and up to our best knowledge, no experimental data for urea adsorption are available in literature. For such reason, this work aims at developing a computational protocol to screen and rank crystal structures, according with their ability to capture urea and other UTs from dilute aqueous solutions.

The screening methodology is based on the characterization of crystal structures available in CoreCOF and CURATED databases [3] by molecular modelling in RASPA [4]. DREIDING force field (FF) [5] was used for LJ parameters of atoms in the frameworks, with partial charges obtained by EQeq and DDEC method. Adsorbate and frameworks were represented as rigid models. A subset of structures was selected based on criteria to ensure safety and stability. Zeo++ was used for a geometrical analysis of pore size, surface area and void volume of the frameworks. The calculation of COFs interactions with urea and other UTs and water at infinite dilution was carried out by Widom's insertion method. The nanoporous materials were ranked considering the binding strength and the selectivity with respect to water [6]. GCMC simulations were employed to assess the quantitative adsorption of water and UTs, enquire the thermodynamics of binding and characterize the binding sites population on a selection of COFs ranked as best candidates from the infinite dilution analysis.

Experimental data of water vapour (298 K) and nitrogen (77 K) adsorption were used to support and to drive the selection of the most appropriate force field to describe adsorption in COFs. Interestingly, adsorption enthalpies and adsorbate binding capacity appeared to be extremely sensitive to frameworks' partial charges selection. DREIDING FF with DDEC charges on the frameworks coupled with single point charge (SPC-E) model for water showed to reproduce experimental water adsorption data the best. Furthermore, the comparison of simulated and experimental isotherms showed discrepancies ascribable to the difference between the crystal structures and the crystallinity of synthesized COFs.

The impact of pore functionalization on organic frameworks revealed to play a fundamental role in the binding properties toward urea at infinite dilution. CONN, IISERP-COF3, CPF-2, TFB-COF, COF-JLU4 and JUC-505 AA from CURATED database showed to the highest excess chemical potential at infinite dilutions, with a wide range of Henry coefficients for water (3 orders of magnitude). Nonetheless, the elemental composition of heteroatoms in the framework structure, pore size, available surface area appeared to be inadequate parameters to describe the urea adsorption. This reveals the complexity of binding phenomena that requires the study of adsorption of mixtures in COFs. The interplay and interactions of the UTs adsorbed showed to be essentially dominated by

$$A = -kT \ln Q$$



electrostatics and dramatically influenced by the water presence that is co-adsorbed in the pore. The proposed approach aims to spot the best candidates for the experimental campaign and devise a quantitative structure-property relationship to describe UTs adsorption. The GCMC simulations results offer the chance to study the mechanism and the binding sites responsible for sorption.

Hypothetical crystals databases, collecting structures not synthesized yet, may provide a huge source of materials to study, providing a larger set for a computational investigation, freed from the synthetic capability. This in-house developed pipeline is a fast, versatile and open-source tool and it will be used in future to drive the design of a new generation of materials for hemodialysis.

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O3.6a Understanding the Relationship between Pore Chemical Environment and Hysteresis using a Genetic Algorithm

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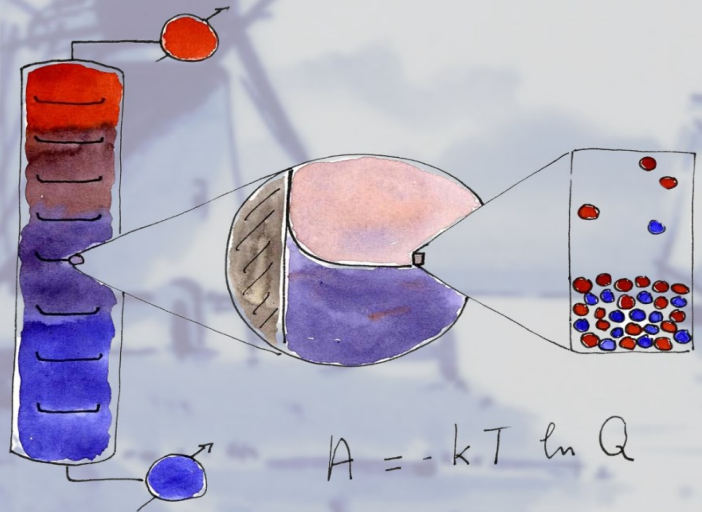
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Porous materials, such as metal-organic frameworks, are promising for many applications including gas storage, gas separation, and water harvesting from air. Adsorption hysteresis reduces the reversibility of the gas adsorption process and affects the overall performance of porous materials as gas adsorbents. Thus, it is desirable to understand the pore chemical environment-hysteresis relationship and optimize the pore to minimize the adsorption hysteresis. However, generating adsorption isotherms for an entire class of materials is infeasible, both experimentally and computationally. Therefore, we propose an *in silico* inverse design approach that uses a genetic algorithm (GA) combined with adsorption isotherm simulations to guide the design of pore chemical environment to enhance the reversibility of the adsorption process through minimizing the hysteresis loop. First, we have designed a model slit pore where we can vary the chemical environment by allowing for various patterns of pore wall beads with different Lennard-Jones parameters. Starting from a collection of random pore patterns, we calculate the adsorption isotherms using transition matrix Monte Carlo (TMMC) methods to assign a fitness value to each pore with smaller hysteresis loops, and therefore more reversible adsorption, implying higher fitness. The GA then evolves the set of pores using the fitness function. The use of a GA minimizes the number of simulations required to explore the chemical space to more efficiently investigate the effect of the pore chemical environment on the hysteresis. Ultimately, insights gained from these experiments can be valuable in designing adsorbents with minimal hysteresis. Here, we will present the results of the GA and discuss insights revealed about the relationship between the pore chemical environment and hysteresis.

Oral Presentations

Session: Aqueous systems



O3.1b Green Solutions for Industrial Efficiency: Predicting Cyrene-Water Mixtures for Sustainable Processes*Callum Donaldson*, Carmelo Herdes*

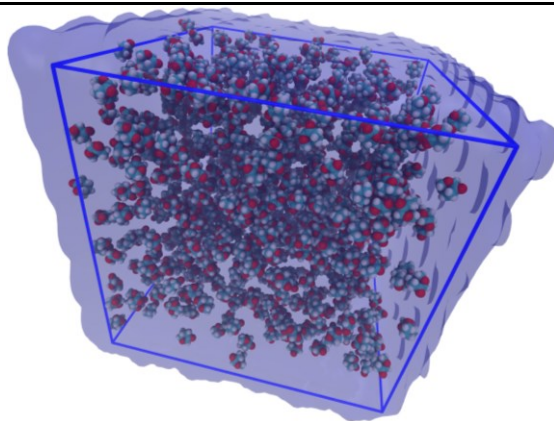
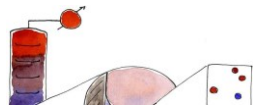
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As industries worldwide strive for sustainability, the search for green alternatives to traditional solvents intensifies. Cyrene [1], a bio-based solvent derived from cellulose-based waste, emerges as a promising candidate due to its low toxicity and renewable sourcing. However, its efficacy hinges on understanding its behaviour when mixed with water, a crucial step for widespread industrial adoption[2, 3].

This comprehensive study combines insights from atomistic and coarse-grained models to delve into predicting the vapour-liquid equilibria (VLE) and transport properties of Cyrene-water mixtures. The AA-OPLS and SAFT-g-Mie potentials are employed to capture fine molecular interactions and offer a broader perspective, respectively. Through meticulous simulations, phase behaviours under various conditions are elucidated, providing indispensable knowledge for process optimization.

Moreover, the selection of Cyrene as a solvent offers additional advantages, such as its compatibility with green chemistry principles and its potential to enhance the performance of sustainable processes. By elucidating Cyrene's behaviour in binary mixtures with water, this research paves the way for informed decision-making in adopting environmentally friendly alternatives. Cyrene's emergence as a green solvent signifies a shift towards greener, more efficient industrial processes, marking a significant step towards a sustainable future. Embracing Cyrene-water mixtures holds promise for revolutionizing industrial practices and contributing to the global transition towards sustainability.



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O3.2b On the possible locus of the liquid–liquid critical point in real water from studies of supercooled water using the TIP4P/Ice model.

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One of the most accepted hypothesis to explain the anomalous behavior of water is the presence of a critical point between two liquids¹, the liquid–liquid critical point (LLCP), buried within the deep supercooled regime. Unfortunately, such hypothesis is hard to be experimentally confirmed due to fast freezing. Here, we show that the TIP4P/Ice² water potential shifted by 400 bar can reproduce with unprecedented accuracy the experimental isothermal compressibility of water and its liquid equation of state for a wide pressure and temperature range. We find, both by extrapolation of response function maxima and by a Maxwell construction, that the location of the model LLCP is consistent with previous calculations^{3,4}. According to the pressure shift needed to recover the experimental behavior of supercooled water, we estimate the experimental LLCP to be located around 1250 bar and 195 K. We use the model to estimate the ice nucleation rate (J) in the vicinity of the hypothesized LLCP experimental location and obtain $J=10^{24} \text{ m}^{-3} \text{ s}^{-1}$ ⁵. Thereby, experiments where the ratio between the cooling rate and the sample volume is equal or larger than the estimated nucleation rate could probe liquid–liquid equilibrium before freezing. Such conditions are not accessible in common experiments with microdroplets cooled at a few kelvin per second⁶, but they could be, for instance, using nanodroplets of around 50 nm radius observed in a millisecond timescale.

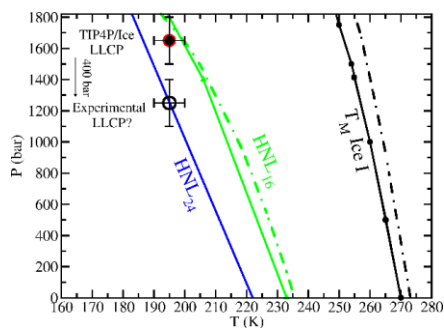
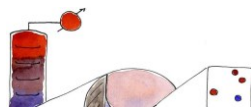


Fig. 1. Pressure-temperature location of the experimental (dashed-dotted) versus the TIP4P/Ice (solid) ice Ih melting (black) and homogeneous nucleation (coloured) lines. HNL subscripts indicate the rate (per cubic meter per second) to which the line of interest is associated. Experimental melting and HNL₁₆ lines are taken from Refs. [7] and [8] respectively. The simulation HNL₁₆ is taken from Refs. [9,10] (except from the 1400 bar point that has been interpolated in this work from those results). The HNL₂₄ line (blue, this work) crosses our guess for the experimental LLCP (empty circle) obtained after shifting 400 bar downward the TIP4P/Ice LLCP (solid circle).

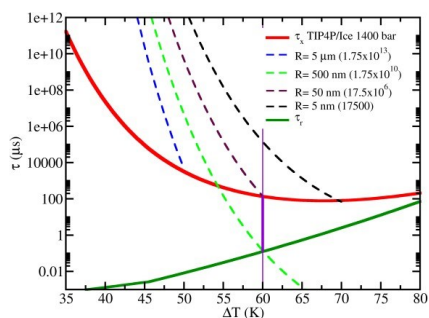


Fig. 2. Time required for nucleating ice (τ_i) within droplets of different radii as specified in the legend (dashed curves) as a function of supercooling for 1400 bar. The estimated number of water molecules for each droplet size is included in the legend. The crystallization time, τ_x (or the time required for 70 per cent of the volume to crystallize) for 1400 bar as a function of supercooling is depicted by a continuous red curve. The relaxation time (τ_r) is represented by a continuous green curve. Finally, the supercooling at which the LLCP could be found, which thickest part indicates the time window available to measure 50 nm water drops in the liquid state.

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O3.3b Exploring the Dipole Moment of Supercritical Water and the Hydrogen-Bonding Contributions Involved

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Supercritical water shows great promise as a new green solvent, with applications in hydrogen generation from biomass and in wastewater treatment. These applications depend crucially on the ability to tune the solvation environment provided by water by manipulating the thermodynamic conditions. In water, the solvation environment is mainly a consequence of the electrostatic, hydrogen bonding, and dispersion interactions between molecules. In the liquid state, a continuous network of hydrogen bonds dominates the fluid structure, but as supercritical conditions are approached and superseded, this network becomes increasingly disrupted. The dipole moment characterizes the electrostatic interactions in the system, and plays a significant role in determining the thermophysical properties of a fluid, particularly its solvation properties and dielectric constant. In the gas phase, water molecules have a dipole moment of 1.85 D; however, in condensed phases, surrounding molecules polarize one another, significantly increasing their dipole moments. Despite its fundamental and practical importance, it remains very challenging to experimentally measure and even theoretically predict the molecular dipole moment in condensed phases, particularly for supercritical states where spacial correlations between molecules are long-ranged.

Recently, we developed the Self-Consistent Electrostatic Embedding (SCEE) method, which is able to accurately estimate the molecular dipole moment in condensed phases with relatively low computational expense. In this approach, classical MD simulations are used to explore phase space in combination with high-level QM/MM methods to compute the electronic properties. We have previously demonstrated its ability to determine the dipole moment of water at ambient conditions, obtaining a value of ~ 2.8 D.¹ This is in excellent agreement with previous ab initio MD calculations and experiment. In this work, we apply SCEE to examine the molecular dipole moment of water across a broad range of conditions, covering the liquid, vapor and supercritical regions. We investigate the



fluid structure and molecular polarization of water, decoupling local and mean-field polarization contributions and providing a clear link between hydrogen bonding and induced dipole moment. We also show that this new physical insight is generalizable to a variety of other compounds, including alcohols and ketones.^{2,3} Finally, we present preliminary work on estimating the static dielectric constant and dielectric response by applying post facto polarization corrections based on the induced dipoles to the predictions of MD simulations⁴.

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O3.4b Variational umbrella seeding for calculating nucleation barriers

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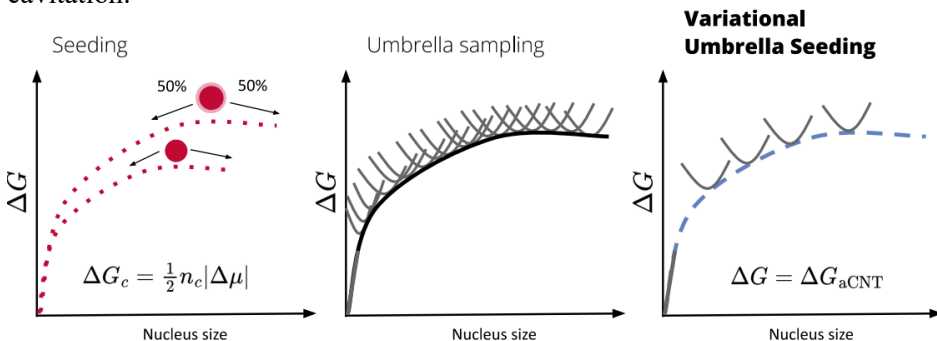
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Nucleation is a phenomenon ubiquitous in both natural and industrial processes. Therefore, the calculation of the rate of nucleation has applications in understanding, predicting and controlling nucleation processes. Although several techniques have been introduced to calculate nucleation rates, most of these require substantial computational resources. As a consequence, most nucleation studies focus on only a few selected state points thereby limiting insights into the pressure and temperature dependence of the nucleation barrier.

Recently, the seeding technique has emerged as an efficient method for calculating nucleation rates, allowing insight into the pressure and temperature dependence of nucleation rates over a very wide range of supersaturation conditions. However, the seeding technique's accuracy is highly dependent on the criterion chosen to measure the size of the nucleus. We introduce a new computational method that overcomes this limitation of the seeding technique. We demonstrate excellent accuracy for crystal nucleation of hard spheres and of two distinct models of water: mW and TIP4P/ICE. This method can easily be extended to calculate nucleation barriers for homogeneous melting, condensation, and cavitation.



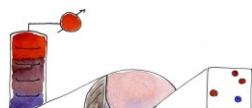


Fig. Schematic comparison of seeding, umbrella sampling, and variational umbrella seeding, illustrating how they estimate the nucleation barrier ΔG as a function of nucleus size.

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O3.5b Equation of State Informed Potentials: Towards a SAFT- γ -Mie based potential for Mesoscopic Simulation

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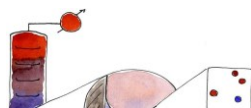
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Colloidal systems have great relevance across many industries, such as personal care, industrial lubricants and biological systems. The characterization of such systems poses a significant scientific challenge due to the length and time scales on which these systems aggregate. This results in traditional molecular simulation unsuitable for the simulation of these systems. At the same time, theoretical approaches are also limited in their description of these systems, due to the complex mesophases that they form, preventing the usage of equations of state which assume homogeneity.

DPD and DPD-like potentials are one potential solution to cross the boundary between the atomistic scale and the mesoscale. While these techniques have been successful in the simulation of mesoscopic systems, the simple form of the potential has its limits. Of note is that these potentials commonly possess a quadratic equation of state. This can lead to unrealistic thermodynamics, for example, the original DPD potential cannot exhibit vapour-liquid equilibrium, which forbids simulations of colloidal systems with a free surface.

In this work we present a new methodology that combines a local density-dependent potential [1,2] with the SAFT- γ -Mie equation of state [3]. This approach results in a potential which retains the numerical advantages of DPD, while at the same time exhibits remarkable accuracy at the mesoscale. The inclusion of the SAFT- γ -Mie EOS also imparts a model of hydrogen-bonding into the model.

We demonstrate that this potential can reproduce the bulk properties of water, including the vapour-liquid equilibrium properties of water to quantitative accuracy. Although the bulk properties of the equation of state potential are excellent, alone, the interfacial properties are not representative of real fluids. This is remedied by the addition of a square-gradient potential, which allows the interfacial properties to be tuned to the properties and in fact, unlike most potentials used in molecular simulation, allows the interfacial properties to be tuned



separately to the bulk properties. This is demonstrated in the surface tension of water being reproduced to a high degree of quality. This work is then expanded to alkanes and alkane-water systems.

It is hoped that this work can be subsequently transferred to quick, efficient and accurate simulation of inhomogeneous systems for the simulation of colloidal systems such as surfactant-oil-water systems, overcoming many of the current limitations of DPD techniques.

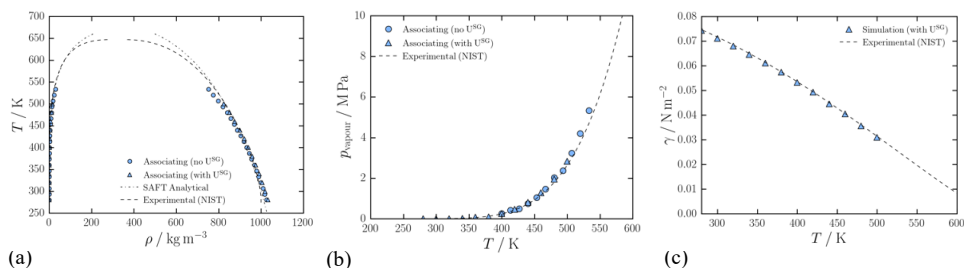


Fig. 1. Thermodynamic properties of water calculated with the local density dependent potential using the SAFT- γ -Mie EOS, with (triangles) and without (circles) the square gradient term, with the experimental values from NIST (dashed line) and the prediction of the EOS (dot dashed line). (a) The coexisting densities of water vs temperature (b) The vapour pressure vs temperature. (c) The surface tension vs temperature.

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O3.6b Prediction of water anomalous properties by introducing the two-state theory in SAFT

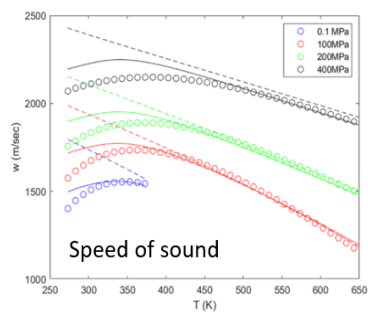
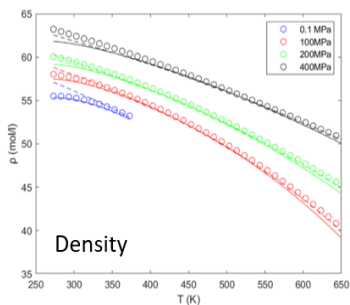
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Water has more than 50 “anomalous” properties (e.g. density maximum, hydrocarbon solubility minimum). The two-state theory, that has gained significant attention due to recent experimental evidence by Pettersson and Nilsson [1], describes water as a mixture of low density (LDL) and high density liquids (HDL), corresponding to different types of water clusters. The existence of LDL and HDL causes an LLE split in subcooled conditions and the anomalous behaviour at the conditions of practical interest to chemical engineers.

We have introduced the two-state theory of water in the Statistical Associating Fluid Theory (SAFT) [2]. We have assumed that water is a mixture (ideal and non-ideal) of two different types of water molecules, HDW and LDW, which are in chemical equilibrium and have different association schemes and association parameters. Using this approach, a generalized association term for SAFT has been derived and incorporated in simplified PC-SAFT EoS [3], resulting in the PC-SAFT-TS (two state) [4]. Several anomalous properties, including density and speed of sound maximum and hydrocarbon solubility minimum, are accurately predicted (Figure 1).



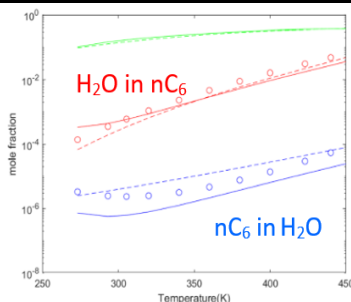


Fig. 1. Prediction of water anomalous properties. Solid lines PC-SAFT-TS [4], dashed lines PC-SAFT [5]

Acknowledgment

The authors wish to acknowledge the VILLUM Foundation for funding this research under the VILLUM Experiment Programme “Is Water a two-state liquid?” (Project No. 49368)

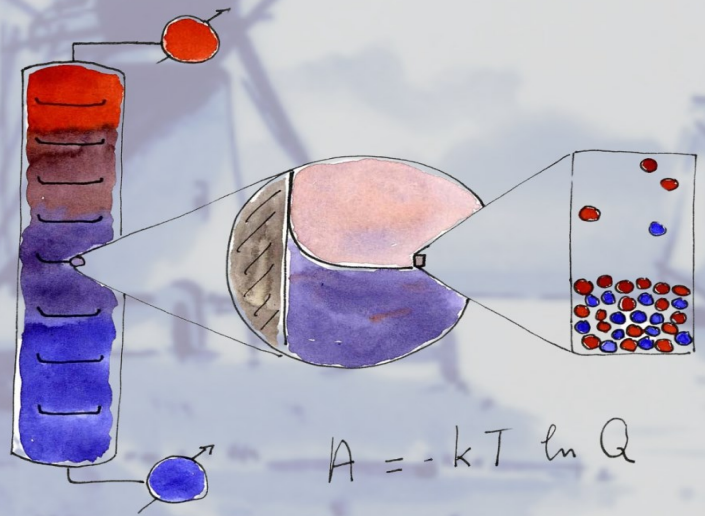
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Oral Presentations

Session: Phase equilibria





O3.7a Brief Overview of Thermodynamic Achievements in the Period 1970 - 2000 at TU Delft

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The Van der Waals theory provided the answer on a number of experimental observations. For instance, the continuity of liquid and gas and the existence of criticality, which was recognized as a combination of attractive and repulsive forces. Also the square gradient theory of Van der Waals was a major contribution to our understanding of interfacial phenomena.

In a second part of the presentation, it will be shown that CO₂ is able together with an ionic liquid to form a miscibility switch that on the one hand it behaves as a solvent suitable to be used for reactions while on the other hand, it can be used to remove the reaction product from the system. This novel technology is very suitable for syntheses in the pharmaceutical industry.

Significant research was performed at TU-Delft in various projects on gas storage in hydrates. Significant financial support was obtained from TU-Delft, Industry and the Global Climate Energy Project from Stanford University. The development of hydrate promoters was published in Science.



O3.8a Phase Behaviour and Density of CO₂ + Toluene + Cyclohexanol Mixtures at T = 293.15 K to 353.15 K and P = 0.1 to 30 MPa

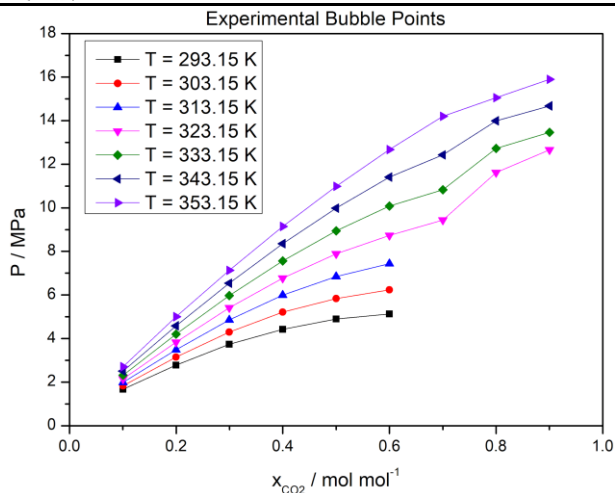
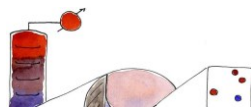
Happiness Imuetinyan^{1*}, Jean-Patrick Bazile¹, Jean-Luc Daridon¹, Cédric Giraudet^{1,2}, and Fabrizio Croccolo¹

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Effective process engineering in various industries depends on accurate and precise experimental data. These data form the foundation for optimising and executing processes efficiently and effectively. Additionally, there has been growing interest in carbon dioxide (CO₂) systems under elevated pressure and temperature conditions because of their significance in sustainability and environmental awareness initiatives, such as carbon capture and storage (CCS) and enhanced oil recovery (EOR) [1]. Investigating the behaviour of CO₂ in combination with other substances, such as alkanes, naphthalenes, and alcohols, is crucial for advancing our understanding of industrial processes and their environmental impact [2].

The phase behaviour and density of the CO₂ + toluene + cyclohexanol ternary mixtures were measured at a temperature of 293.15 K to 353.15 K and at pressures ranging from 0.1 MPa to 30 MPa. Measurements were performed in a toluene/cyclohexanol (30 wt%/70 wt%) mixture and 11 different mixtures, with CO₂ molar fractions ranging from 0.1 to 0.9. Using a synthetic and visual approach, saturation pressures ranging from 16.69 to 158.95 bar were obtained by employing an adjustable volume high-pressure cell to measure bubble and dew point pressures through the visual detection of phase transitions at a constant overall composition. The density data were acquired using a vibrating U-tube densimeter. The findings obtained from this study demonstrate the existence of liquid-liquid immiscibility within the examined temperature range and at a mole fraction of CO₂ greater than 0.6. The system under study probably exhibited type IV phase behaviour, as classified by Van Konynenburg and Scott. To the best of our knowledge, this is the first time that phase equilibria and density measurements have been performed in this ternary system.



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O3.9a Liquid-Liquid Phase Split of Associating Polymer Mixtures*R. Bergmann, S. Enders**

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With increasing interest in healthy lifestyles and protection of the environment in the recent years, plant-based meat substitutes have gained more significance in society and research [1]. The primary process for achieving this is extrusion, aimed at replicating a fibrous structure and texture closely resembling meat. However, it remains challenging on a more fundamental level to understand the interactions during extrusion processing related to the transition of the protein molecules or -phase into those fibrous structures, which is considered a “black box” with scarce information inside [1]. Furthermore, understanding the extrusion process, which involves the use of diverse protein-rich raw materials (e.g., from various plant sources) with varying material properties, poses a significant challenge [2]. From a thermodynamic perspective, the phase separation behavior of the protein-rich raw materials is the key factor in understanding the process. One approach to model the miscibility gap of polymer blends is through lattice theories like the Lattice Fluid Theory by Sanchez and Lacombe [3]. However, this thermodynamic model in its original form does not consider the association interaction, which occurs in proteins and can have a large impact on the phase behavior. Therefore, we incorporate the association interaction into the Lattice Fluid Theory using different approaches, like the extension suggested by Panayiotou and Sanchez [4] or the Extended Chemical Association Lattice Model (ECALM) by Browarzik [5]. The contribution discusses the advantages and disadvantages of both models regarding the calculation of the phase separation behavior of associating polymers. The calculations were performed using model polymers with associating functional groups, for instance, polymers produced from lactic acid. The calculated miscibility gaps were compared with experimental data taken from the literature.

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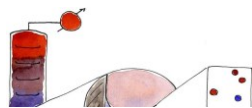
O3.10a Automated Model-Assisted Phase Behaviour Measurements

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Understanding the thermophysical properties of fluids is crucial to the effective development of industrial processes and is dependent on models optimised against reliable experimental data that are often in short supply. Knowledge of the fluid phase behaviour is especially important, yet these measurements are challenging and time consuming. As such, there is significant incentive to improve the procedure and design of experiments, providing an opportunity to put the thermodynamic models being optimised to use as an experimental aid supporting automation. While the implementation is not trivial and must be done with care, it allows for measurements to be made more rapidly and in a more reproducible fashion, benefitting from machine precision. Such an approach has been realised in an automated static-analytical apparatus, wherein the capability to inject and vent fluids, a rigorous data acquisition and control program, and a Peng-Robinson model allow for careful movement through the phase space. Varying degrees of automation have been applied successfully to measurements of mixtures of isobutane + H₂ and methanol + CO₂, and further refinements have been identified. While the apparatus currently follows a path determined a priori and relies on dead reckoning, and thus is subject to the accumulation of deviations, it is possible to have more adaptive approaches suitable also for mixtures displaying initially unknown behaviour. The further development of model-assisted autonomous systems shows promise not only for phase behaviour, but for a wide range of multiphase property measurements.



O3.11a Benchmarking the Predictive Capabilities of the SAFT- γ Mie Eos for Properties of Interest in Pharmaceutical Systems

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Thermodynamic molecular models are essential in the development and manufacturing of active pharmaceutical ingredients (APIs) as they provide detailed insights into the physical and chemical properties of compounds under process conditions. By accurately incorporating the interactions of APIs with solvents, excipients, and other formulation components, predictive models aid in designing efficient synthesis and purification processes, thereby reducing production costs and minimizing waste. Among these models, equations of state (EoS), particularly those based on the statistical associating fluid theory (SAFT), have proven effective in predicting the properties of API-related systems.

In this work, we carry out a benchmark study of the accuracy, reliability, and predictability of the SAFT- γ Mie EoS [1] in describing the properties of systems relevant to the pharmaceutical industry. The recent advancements in the SAFT- γ Mie EoS are reviewed [2-7], and an updated parameter matrix is presented. We compare the properties of binary API-solvent and ternary API-solvent-solvent systems predicted by the SAFT- γ Mie EoS with experimental data reported in the literature. We consider 9 APIs, 9 amino acids, and 26 solvents, examining properties such as solid-liquid solubility in pure (as shown in Figure 1) and mixed solvents, octanol/water partition coefficient, pH-dependent solubility, and phase equilibrium (SLE, SLLE, LLE, and VLE). Additionally, the predictions of the SAFT- γ Mie model for these properties and systems are compared with other models including but not limited to the UNIFAC model.



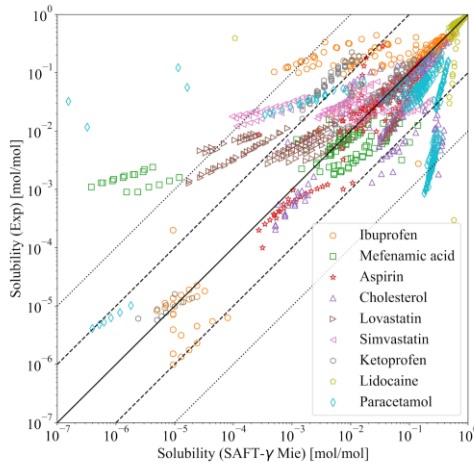


Fig. 1. Parity plot of the solubility of the APIs in selected solvents.

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O3.12a On the Compatibility of Butanol + Water + Dimethyl Carbonate blend at its Vapor-Liquid-Liquid Equilibrium.

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The energetic transition to sustainable and renewable energy sources requires partial or total substitution of fossil fuels for a combination of solar, wind, hydrogen-based and/or biofuel-based energy sources contributing to the energy grid. From those sources, biofuels have the advantage of being completely renewable and compatible with current combustion technologies. From the existing products, bio-butanol blended with other oxygenates, such as cyclopentyl methyl ether [2] for gasoline engines or dimethyl carbonate (DMC) [3] for diesel engines, are claimed to be a promising full replacement to fossil fuels. However, the bio-butanol synthesis is carried out in aqueous media therefore, it is mandatory to characterize the thermodynamic behaviour of bio-butanol hydrated blends to evaluate the final fuel viability.

To contribute to the thermodynamic evaluation of the butanol hydrated blends, this work is focused on the case of the butanol + water + DMC ternary mixture. Specifically, this work reports experimental measurements and theoretical modelling for vapor-liquid-liquid equilibrium (VLLE) at atmospheric pressure. From Figure 1, it is possible to observe that this ternary mixture displays a zeotropic behaviour, where its three-phase line connects two heterogeneous azeotropes found in its sub-binary mixtures. Experimentally, it is observed that the two liquid phases at equilibrium show a barotropic (density) inversion close to the water + DMC heteroazeotrope and the presence of both butanol and DMC favors the mutual solubilities of water and organic phases. The observed experimental determinations are predicted from SAFT-VR-Mie EoS which only uses pure fluid and binary interactions. According to the theoretical results, this molecular based EoS accurately reproduces the shape of the overall ternary phase equilibrium.



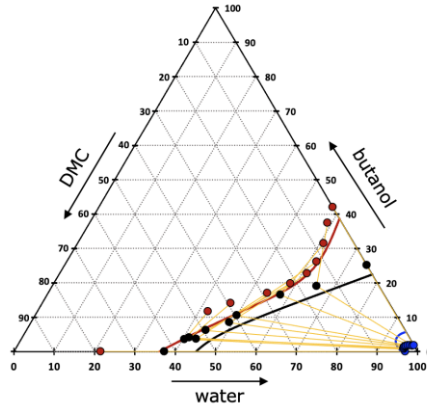


Fig. 1 – Water + Butanol + DMC VLE. Red, blue and black colors represent organic, aqueous and vapor phase, respectively. Dots are experimental measurements connected via yellow tie-lines and red, blue and black lines correspond to SAFT-VR-Mie predictions.

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O3.13a ThermoQuiz: Game-based learning of basic thermodynamic principles

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Over the last years, the HeatQuiz project has gained considerable amount of attention [1]. HeatQuiz is an open access platform providing the full study material for heat transfer course on Bachelor level (www.heatquiz.app). With more than 1.350 million questions solved over the past four years, the course concept has been applied to support the education of thousands of students at RWTH Aachen University, the University of Twente and the Vrije University of Amsterdam.

Based on the same conceptual idea the open access teaching platforms, ThermoQuiz, FlowQuiz and MechQuiz have been initiated at the University of Twente over the last two years. Although, the learning path for ThermoQuiz is continuously under development, it provides already access to multiple short video lectures, and contains more than 380 quiz questions (see <http://167.86.98.171:3004/playcoursemap/97>) Note, more than 64.000 questions have been solved by students from the University of Twente so far.

The presentation will introduce the concept of HeatQuiz and ThermoQuiz, including the different question types that have been specifically designed for these courses. This includes a tool to train students in the basics of balances as well as drawing tool for the basics of thermodynamic cycles.

Furthermore, we will critically address and discuss the benefits and problems that arise with students in a course that is dedicated to self-regulated learning. These problems include for instance a low attendance rate during classes and tutorials due to the availability of the entire teaching material as well as a strong polarization of low and high performance in the final examination.



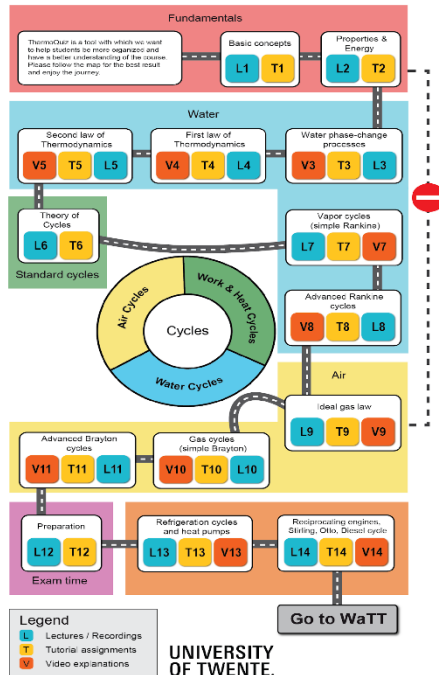
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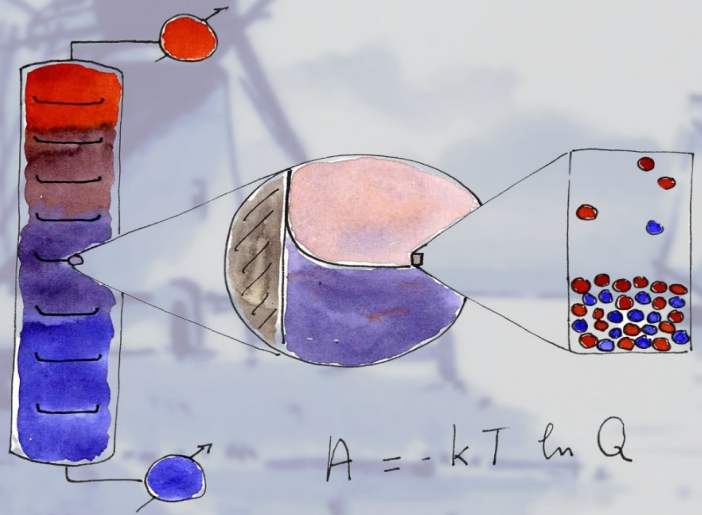
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$$A = -kT \ln Q$$

Oral Presentations

Session: Thermodynamic modeling
at different scales



$$A = -kT \ln Q$$

O3.7b Local equilibrium in liquid-phase shock waves?

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A shock wave is clearly a non-equilibrium process when used on a macro scale such as in explosions [1], disintegration of kidney stones [2], and explosive welding [3]. There are few examples of shock-wave analyses using linear non-equilibrium thermodynamics (NET), probably because the forces and fluxes are so large. On the other hand, in computer simulations much higher fluxes and forces are used seemingly satisfying the linear regime. Two central questions in the assumption of local equilibrium are (i) what is “local” and (ii) how valid is the assumption? If the local-equilibrium assumption is valid, NET can be used in analyses of the shock front, e.g. how energy is converted there. In this work, we analyze results from molecular dynamics simulations (NEMD) and numeric solutions of the Navier-Stokes (N-S) equations for a planar shock with Mach 2 in a Lennard-Jones/spline liquid.

By comparing results from NEMD with equilibrium simulations (EMD) and an equilibrium equation of state (EoS), we found that the local-equilibrium assumption is a very good approximation when shock-front properties were recorded in molecular-scale bins [4]. We also found that N-S results were in good agreement with the NEMD data [4].

This conclusion was supported by the agreement between results for the excess entropy production in the shock front, computed with four different methods that used the local equilibrium assumption in different ways. Two of the methods assumed local equilibrium between excess thermodynamic variables by treating the shock as a surface in Gibbs’s sense [5,6]. The other two methods were based on the local equilibrium assumption in a continuous description of the shock front. We found that all four methods give excess entropy productions that are in excellent agreement for the shock studied in this work.

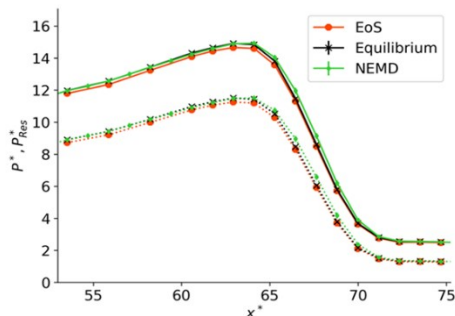
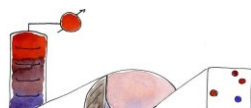


Fig. 1. Comparisons between pressure results from NEMD, EMD, and EoS as function of position in the wave front. The upper and lower plots are the total and excess pressure, respectively. The numbers are in Lennard-Jones units.

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O3.8b Investigation of the Co – TiO₂ Interaction in Fischer-Tropsch Synthesis through Multi-Scale Simulation Studies

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The Gas-To-Liquid (GTL) process, based on Fischer-Tropsch synthesis (FTS), has garnered significant attention from both academia and industry. Research efforts have been directed toward optimization of various parameters, including the catalyst (cobalt nanoparticles) and its support (TiO₂). Understanding the interaction between the catalyst and TiO₂ is crucial for enhancing the catalytic process and enabling further advancements, including catalyst optimization.

This research work focuses on the development of an effective molecular potential to describe the interaction between cobalt (Co) and titanium dioxide (TiO₂), the primary support material for cobalt-based FTS catalysts. The emphasis is on understanding the behavior of cobalt nanoparticles on the FTS support, with a particular focus on the sintering process of the catalyst.

To establish a robust molecular potential, quantum mechanics calculations were utilized as reference data for fitting the force field. This approach allows for a more accurate representation of the complex interactions between cobalt and the TiO₂ support. Furthermore, to capture the challenging nature of transition metal systems within standard Density Functional Theory (DFT), a systematic investigation using different DFT functionals has been performed. This comprehensive analysis aims to identify the most suitable DFT approach for modeling the cobalt-TiO₂ system, ensuring reliable and accurate results [1].



The ultimate goal of this work is to enhance the understanding of how cobalt interacts with the TiO_2 support, and thus, develop strategies that can improve catalyst activity, stability, and overall performance in FTS applications.

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O3.9b Application of the Kirkwood-Buff solution theory to solid solutions*Jean-Marc Simon*^{1*}, Peter Krüger² and Masafumi Miyaji²¹ICB, CNRS-Université de Bourgogne, 21000 Dijon, France, ²Graduate School of Science and Engineering, Chiba University, Chiba 263-8522, Japan

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The aim of this work is to apply the Kirkwood-Buff solution theory [1,2] to solid solutions. Different compositions of Xe-Ar solid solutions (Xe rich) were simulated using Monte-Carlo simulation at 84-85K [3]. The pair distribution function and the Kirkwood Buff's Integrals (KBIs) were computed giving the possibility to access to thermodynamics quantities like the chemical potential and the partial molar volume. Margules activity models were fitted to the results and extrapolated to the full range of mole fraction. The model was used to predict the conditions where the solution is thermodynamically stable and the result agrees well with experiment.

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O3.10b How to compute density fluctuations at the nanoscale

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Thermodynamics is a macroscopic theory. To describe physical chemistry properties of complex systems such as confined fluids at the nanoscale, it is useful to generalize thermodynamics concepts to nanometre sized systems. Different approaches have been suggested to this end, most famously Hill's thermodynamics of small systems [1], which was further developed as the so-called small system method by Schnell et al. [2]. Using this method, intensive variables such as the pressure and the isothermal compressibility κ_T have been calculated for finite open volumes V in a homogeneous fluid. It was found that κ_T varies strongly with V and scales as $V^{-1/3}$ in the limit $V \rightarrow \infty$. As an example, the compressibility of liquid water in an open volume containing some 100 molecules was found to be about twice as large as the bulk value [3]. I argue that such a large size dependence of κ_T is unphysical and that it must be considered an artefact of the computation method, where κ_T is obtained from the number fluctuations of point-like particles in a finite open volume V .

Here I study the compressibility of hard sphere fluids (HSF) in 1D and 3D as a function of system size. In 1D, where exact results are known [4], κ_T is strictly size-independent. I show that the correct result is also obtained when κ_T is computed from the volume fluctuations in the isobaric ensemble for any system size. However, when κ_T is computed from the particle number fluctuations in a finite open system, a large size dependence is found as in Ref. [3] in stark contradiction to the exact result. I show that the problem is due to the neglect of the excluded volume of the particles, which are taken as point-like in the standard statistical mechanical definition. I propose a modified radial distribution function (RDF) which takes account of the finite size of the particles through an internal density. For spherically symmetric density profiles, the modified RDF can be obtained from the usual, point-like RDF by a simple one-dimensional convolution. Analytic formulae are given for hard-sphere particles [5] and for particles with a gaussian density profile. Importantly, the modified RDF yields identical results as the usual RDF in the thermodynamic limit $V \rightarrow \infty$. When κ_T is computed from the

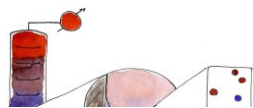


number fluctuations with the modified RDF, the system size dependence is dramatically reduced. It can be made to vanish by a suitable choice of the particle diameter σ that is used in the definition of the RDF. In the 1D HSF at large filling, this value of σ coincides with the hard-sphere diameter. In other cases, σ may be considered an adjustable parameter, which is chosen such as to make the compressibility size-independent in the homogeneous fluid in agreement with the exact result for the 1D HSF.

Based on these findings, I argue that the local compressibility $\kappa_T(\mathbf{r})$ in an inhomogeneous fluid can be defined in a physically meaningful way via the local particle density fluctuations, provided the latter are computed with the modified RDF and finite volume Kirkwood-Buff theory [6,7].

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O3.11b On How to Measure the Subdivision Potential in Nanothermodynamics

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We discuss a central concept of nanothermodynamics [1,2]; the subdivision potential [3]. We explain how it can be measured or calculated for some typical ensembles, as this has been disputed in the literature. We proceed to discuss its meaning for particular systems and predict scaling laws for three ensembles. The laws depend on the small system geometry in a predictable way for an ideal gas model with surface adsorption. We provide new equations which relate the subdivision potential to experimental investigations, and give expressions for grand canonical ensembles of spheres, cylinders, slit pores and fluids confined in porous media. The subdivision potential is not compatible with the popular Hadwiger theorem in geometry and can therefore not be described by a Minkowski set of variables. It is equivalent to Gibbs descriptions when shape- and size variables are defined.

Acknowledgement

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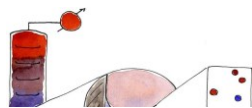


O3.12b Prediction of CO₂ solubility in semicrystalline polyethylene and the influence of molecular architecture*Jana Zimmermann¹, Sabine Enders², Michael Fischlschweiger^{1*}*¹Chair of Technical Thermodynamics and Energy Efficient Material Treatment,
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The solubility of CO₂ in semicrystalline polymers plays an essential role in various industrial applications, including recycling techniques such as supercritical fluid extraction [1] and gas separation via membranes [2]. The gas solubility can be significantly influenced by the molecular architecture and morphology, in terms of the mean degree of crystallinity and the shape of the crystalline domains. Consequently, experimental data in the literature often exhibit a wide degree of scatter. To investigate molecular architecture-morphology-gas solubility relationships, it is important that experimental data sets are available which provide information on gas solubility as well as on molecular architecture and morphology. These data then provide the foundation to deeper understand the gas solubility of CO₂ and subsequently to model gas solubility in the semi-crystalline region in a fully predictive manner.

In this study, the CO₂ solubility in two grades of polyethylene, linear low-density polyethylene and high-density polyethylene respectively, is predicted. For this purpose, a thermodynamic-mechanical model [3] based on the eigen pressure approach [4,5] and the Sanchez-Lacombe [6] equation of state is applied. Additionally, the model also considers the temperature-dependent morphology of the semicrystalline polyethylene, which enables a successful prediction of gas solubility. To validate the model, the molecular architecture and morphology of the polyethene grades, as well as the CO₂ solubility, are investigated experimentally, such that a molecular architecture-morphology-CO₂ solubility-relationship is developed. The investigations have demonstrated that for this system, the gas solubility is dependent upon the bivariate molecular architecture of the polymer, i.e. molecular weight distribution and branching distribution, in addition to the morphology. Furthermore, the thermodynamic-mechanical model has been shown to be capable of accurately predicting gas solubility in the semicrystalline state.



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O3.13b Stretching of nucleotide strains in the isometric- and isotensional ensemble*Sondre K. Schnell*^{*}, Arpenik Kroyan

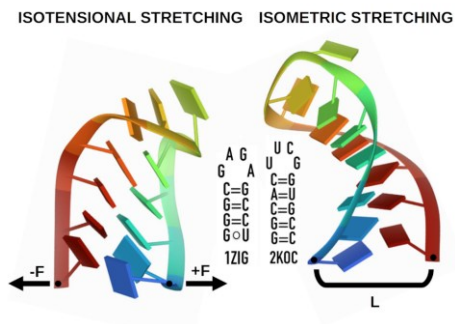
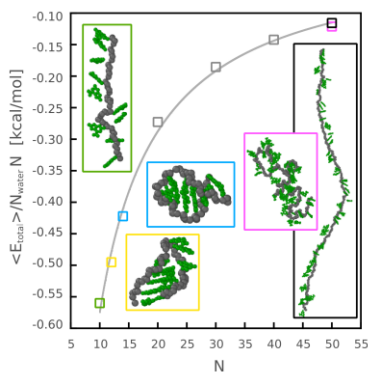
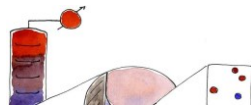
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Thermodynamic properties of short strains of polymer can depend on the shape and length of the polymer strain. These small strains are biologically important, and there are still many un-answered questions about their structure, the energetics of folding/unfolding, and changes in Gibbs and Helmholtz energy, as well as irreversible work during the stretching.

In the isotensional- and isometric ensemble, the terminal end of different polymer strains is stretched with either constant velocity or with constant stretching force. The system is viewed within the framework of Hill[1, 2], and is considered a small system in the thermodynamic sense. In this work, we consider the stretching of mono-nuclear strings from 5 to 50 nucleotides long, as well as two hairpin-loops (1ZIG and 2KOC) in vacuum and in a liquid water model.

The model shows the system is size-dependent, and longer strains shown less size-dependence. In the long-term limit, the system converges to the thermodynamic limit. In addition, the model polymers have enhanced small-system effects when the stretching is performed in vacuum, rather than in the water model. This emphasise the effect of the water layer around the string, and how the interaction with the water molecules reduce the size effect.



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O3.14b Simulation of a Fruit Juice Concentration Process Utilizing Hydrate Technology

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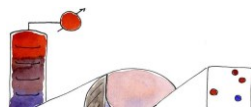
Hydrates are solid crystalline substances formed when water molecules self-organize themselves under specific conditions of high pressure and/or low temperature. This physical phase-change process creates a solid framework with internal void spaces (cages/cavities), which are often filled with gas molecules like methane, ethane, or carbon dioxide, maintaining the structure's stability (Sloan & Koh, 2007).

The solution-concentration method using hydrate technology relies on the fact that solid particles in the solution do not become part of the hydrate's crystal structure during formation, allowing for efficient concentration of the solution via water capture/removal (Li et al., 2015).

The use of hydrate formation for juice concentration offers two key benefits: it retains a higher amount of bioactive compounds and consumes less energy compared to traditional methods (Seidl et al., 2019). This technology has the potential to promote sustainability and serve as an alternative to current juice concentration practices.

The current study delves into both the technical and economic aspects of hydrate-based juice concentration through computational analysis, comparing it with established industrial methods. For the base case, carbon dioxide is used as a hydrate formation gas.

The kinetic behaviour of hydrate formation is studied and a kinetic correlation is extracted to simulate the process. Then, the process is designed in simulation software and juice concentration results are obtained. By means of parametric analysis and based on thermodynamic constraints, suitable operating conditions are obtained and a preliminary calculation of energy requirements is made. Additionally, the utilization of various gases and organic solvents including ethane and propane for hydrate formation is also studied in this context.



Reference

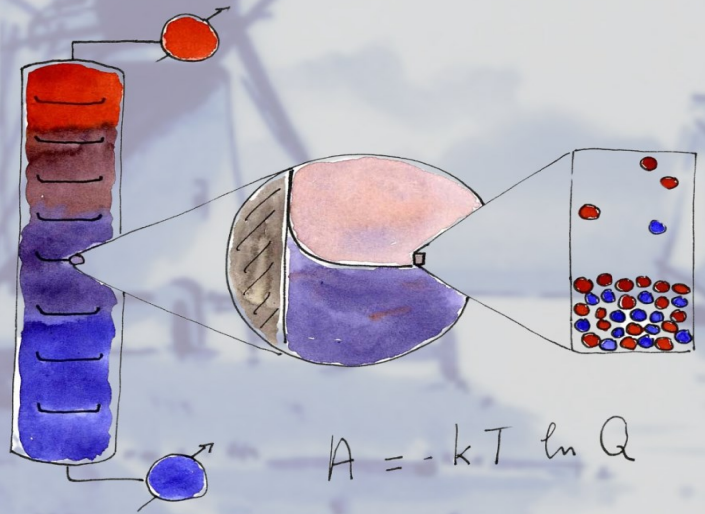
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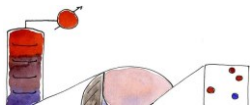
Poster Presentations

Day 1

P1.1 – P1.32



$$A = -kT \ln Q$$



P1.1 Screening of Metal Organic Frameworks for paraffin/olefin separation synergizing molecular simulation, machine learning, and active learning

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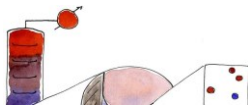
Production of highly pure ethylene (C_2H_4) and propylene (C_3H_6), a significant energy source and crucial raw material in the petrochemical sector, requires the separation of ethylene from ethane (C_2H_6) and propylene from propane (C_3H_8). Metal-organic frameworks (MOFs) are crystalline nanoporous materials that are being discovered at an exponential rate because of their high tunability, porosity, and supernatural surface area, with over a million structures having been synthesized experimentally and another eight million constructed insilico till now. Due to their unique dual organic and inorganic nature, these materials establish a sweet spot for adsorption-related applications and show prominence over traditionally used energy-intensive cryogenic distillation for efficient gas separation. In light of the fact that so few of the many potential MOF structures have been found so far, exploring the vast design space of MOFs by utilizing the framework of high throughput computational screening (HTCS) for a material that excels in the application at hand is like looking for a needle in a sawdust haystack. In this work, we take advantage of the resources provided by big data science by combining machine learning (ML) techniques with HTCS due to the latter's scalability and resilience to screen $\sim 23,000$ hypothetical MOFs for paraffin (C_2H_6 and C_3H_8) selective separation. To prevent unnecessary computation time, MOFs with undesirable properties were first removed by structure-based pre-screening. MOFs passing the structure check were then subjected to multi-component grand canonical monte carlo simulations (m-GCMC) to obtain adsorption capacity and selectivity of olefin/paraffin (C_2H_6/C_2H_4 and C_3H_8/C_3H_6) mixtures. Further, the structure-property relationships between separation metrics and structural features were established, revealing a tradeoff between uptake and selectivity. Next, we deployed nine supervised ML algorithms to learn the relationships between



features describing MOFs and separation metrics. The best ML model, thus obtained in each case, was coupled with recursive feature eliminations (RFE) and hyperparameter optimization (HO) to screen the remaining materials. Additionally, active learning (AL), an efficient and cutting-edge machine learning technique, was used to further enhance the inadequate olefin/paraffin selectivity prediction. The superiority of the latter was then established by comparing the top materials predicted by both approaches. Furthermore, to understand the underlying physics governing olefin/paraffin separation, feature importance was evaluated using permutation importance and the shapely additive explanations (SHAP) technique was applied to estimate the positive and negative influence of features on target property. The simulated and ML predicted properties of the top materials were then compared to validate the ML models. Additionally, these materials were compared to those previously reported, demonstrating that the proposed ML-assisted HTCS is efficient and effective. The hierarchical strategy devised in this study will facilitate the quick screening of MOFs across multiple databases towards industrially significant separation processes by leveraging molecular simulations and machine learning^{1,2}.

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P1.2 Metal Organic-Framework Transparency to Water Interactions for Enhanced CO₂ Adsorption

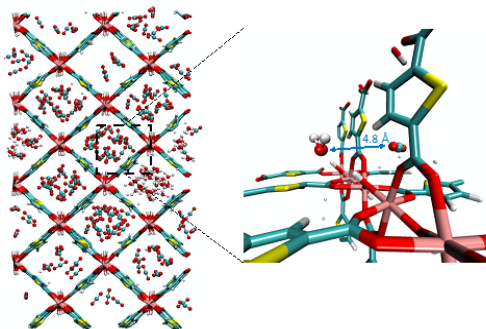
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Today, the capture of post-combustion CO₂ has become a global priority, particularly in order to curb rising temperatures in the coming decades. CO₂ physisorption in porous materials such as Metal-Organic Frameworks is likely one of the most effective approaches to addressing this problem, thanks to its low energy requirement and improved regeneration process. In this study, I investigated CO₂ capture in humid conditions using the Al-MIL-53-TDC metal-organic framework through molecular simulations. I observed that water filling occurs

gradually through pore capillary condensation. Remarkably, the presence of water (at a hydration rate of 4.4 wt%) resulted in a significant increase of 283% in the adsorbed amount of CO₂ (1.8 mmol/g at 0.2 bar) due to a unique transparency property. The thin molecular walls between the uniaxial channels enable van der Waals and electrostatic interactions between water and



adsorbed gas, which allow media on opposite sides of the walls to influence each other. The increase in isosteric heat of adsorption (46 kJ/mol) is attributed to the contribution of water/water energy resulting from the truncation of the hydration shell of water. This truncation increases the number of hydrogen bonds, which can be linked to a kosmotropic effect. Additionally, the selectivity of hydrated Al-MIL-53-TDC for CO₂/N₂ increased by 185% at 0.2 bar (composition 20:80), compared to the unhydrated MOF material with Q_{ST} < 50 kJ/mol.



P1.3 Computational Insights into some Amino Acid-based Ionic Liquids: Unraveling Structure and Dynamics through Quantum Calculation and Molecular Dynamics Simulation

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Ionic Liquids (ILs) have very promising properties, such as tunability of cation and anion and wide electrochemical windows with numerous applications, including gas separation and capture of CO₂. Amino acid-based ionic liquids are known to have high biodegradability and low toxicity compared to traditional ILs. In this context, we are interested in the structural and transport properties of few amino acid-based ionic liquids using the density functional theory and classical molecular dynamics simulation. The ionic liquids consist of cyclic alkylammonium (Pyrrolidinium and piperidinium) cations and amino acid (Lysine, Histidine, Arginine) anions. The Natural Bond Orbital (NBO) and the Atoms in Molecules (AIM) analyses gave a deeper understanding of the interactions and H-bonding between the cation and anion. Various static and dynamics properties such as Radial Distribution Function, Diffusion Coefficient, Hydrogen Bond Dynamics of ion pairs, affecting the viscosity of the ILs have also been investigated.

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P1.4 Mesoscale Modelling: Simulating Pluronic L64 with Dissipative Particle Dynamics

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Dissipative Particle Dynamics (DPD) is a mesoscale tool bridging the gap between microscopic atomistic simulation and macroscopic thermophysical modelling. DPD has become highly popular for studying self-assembling polymer and surfactant solutions where the interactions can be mapped to the Flory-Huggins parameters¹. This research builds upon a preliminary study performed by Droghetti et al.², which used a DPD model with parameters sourced from existing literature^{1,3} to simulate water mixed with Pluronic L64. This study aims to evaluate the effectiveness of DPD models in replicating Pluronic-water combinations in demonstrating the transferability of these parameters. By utilising these parameters previously tested for Pluronic L64⁴, this study successfully simulates mixtures of water with Pluronic L64 in new concentrations; see figure below for more details, achieving good agreement with experimental results⁵. The analysis focuses on identifying cluster structures and characterising them through parameters such as radius of gyration, aggregation number, and cluster mass distributions.

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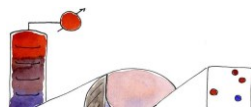
P1.5 Understanding water and ion transport via functionalized nanopores in 2D hexagonal boron nitride using molecular dynamics simulations

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Two-dimensional (2D) materials, consisting of a few atomic layers, are extensively researched for various applications, including seawater desalination. These materials can be engineered to contain nanopores, whose size, shape, and chemical character significantly affect the material's performance as a membrane. Accordingly, nanoporous 2D materials and their functionalized forms have emerged as promising membrane materials for water desalination applications due to their remarkable mechanical strength, high water permeance, and excellent selectivity. In this regard, recent studies have demonstrated that the chemical functionalization of nanopores in graphene (for example, by adding hydroxyl groups) can enhance water permeability and provide 100% rejection of salt ions. In this work, we examine both functionalized and unfunctionalized nanoporous hexagonal boron nitride (hBN) membranes for desalination with different salt solutions via molecular dynamics (MD) simulations. Our MD simulations reveal a significantly higher water permeance through hBN membranes, as compared to the typical water permeance of current polymeric membranes, which is around $0.1 \text{ L.cm}^{-2}.\text{day}^{-1}.\text{MPa}^{-1}$. We find that functionalized nanopores in hBN (with H, O, and OH groups at the edges) demonstrate a slightly lower water flux and higher overall ion rejection, as compared to unfunctionalized nanopores. Moreover, by studying ions of various charges and sizes, our study unravels the complex interplay between ion characteristics and membrane functionalization and their effects on the desalination performance of nanoporous hBN membranes. These findings have significant implications for the advancement of membrane technology, as they offer valuable insights that can be leveraged to design improved membranes for more efficient water desalination processes.



P1.6 Thermodynamics of aqueous salt solutions

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The thermodynamic properties of salt solutions can be described in principle using a G^E model or an equation of state. In the case of aqueous salt solutions different G^E models and different equations of state are present in the literature.

The widely used G^E models are the famous Pitzer model¹ or the e-NRTL². Both approaches consider the electrostatic interactions and the dispersion forces. Different problems occur if also polymers are present in the mixture because the reference states are different. To solve this problem, an alternative approach based on the Pitzer model was developed³. The alternative consists of the use of the standard state of ideal-athermic mixtures, which is usually used for polymer-containing mixtures. The change of the standard state requires a completely new parameterization of the model⁴.

On the other hand, different equations of state for electrolytes were developed in the literature, for instance, the WSW-EOS⁴ or the extension of the cubic plus association (CPA) EOS^{5,6}. The physical base for the WSW-EOS⁶, **Error! Bookmark not defined.** is the description of the electrostatic interactions using a mean spherical approximation combined with a Born-term and the description of the dispersion part by applying the Peng-Robinson-EOS⁷. In contrast, the extended CPA used the Debye-Hückel approach combined with a Born-term for the electrostatic interactions and the Soave-Redlich-Kwong EOS⁸ or the dispersion interaction.

In this contribution, three models, namely the alternative Pitzer model, the WSW-EOS, and the extended CPA were used to calculate different properties of aqueous salt solutions. In the case of the EOSs, we start with the properties of pure water (vapor pressure, densities of the liquid and vapor phase, heat of evaporation, isobaric heat capacities of the saturated liquid and the saturated vapor). All models were used for the calculations of the properties of aqueous salt solutions including osmotic coefficients, activity coefficients, liquid densities, apparent molar heat capacities, and salt solubility. All properties are investigated as a function of salt concentration and temperature. The calculated physical properties will be compared with experimental data taken from the literature. We will discuss the



advantages and shortcomings of every used model, where a special focus lies on the temperature dependency of the physical properties.

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P1.7 Altering interfacial thermodynamics of methanol water solutions at the A-scale to yield separations beyond the thermodynamic limit using nanoporous graphene.

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Membrane separations have been shown to be promising alternatives for separations of liquid solutions, which otherwise require highly energy expensive and thermodynamically inefficient processes for the same. However, a drawback of these membranes is considered to be their permeation flux, which is significantly lowered due to the diffusive time-scale of the solute/solvent in the membrane.

2-D nano porous materials are essentially taking the idea of membranes to the atomic limit. Since the size of the nanopore is of the order of the atomic length scale, they induce local structural and dynamical changes at the interface. This, when applied to the evaporation problem, have shown that the use of functionalized nano porous graphene can enhance the room temperature evaporative flux of water 30-fold, by altering the local interfacial thermodynamics and relaxation dynamics^[1].

Advancing on these findings, we employ the use of functionalized nano porous graphene to study the room temperature evaporation for multiple composition of methanol water solutions. It is found that: ^[2]

- Beyond a composition of 35 mol% methanol, the nano porous graphene is fully selective to the evaporation of methanol. (fig.1).
- The evaporative fluxes of methanol in all cases are enhanced by a factor of 4 ~ 6
- The nanopores in the graphene cause a local demixing of methanol and water, leading to the formation of a methanol enriched interface on the vapor side of the FNPG.
- The distribution of interfacial structures in the case of the bare interface and beneath the pore are significantly different, with higher cluster sizes being observed in the vicinity of the pore.
- The functionalization of the pore leads to slowed interfacial water cluster dynamics beyond 35 mol% methanol, reducing the rate of generation of free



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water three to fourfold (fig 2). This causes the near-complete suppression of water evaporative flux beyond this composition.

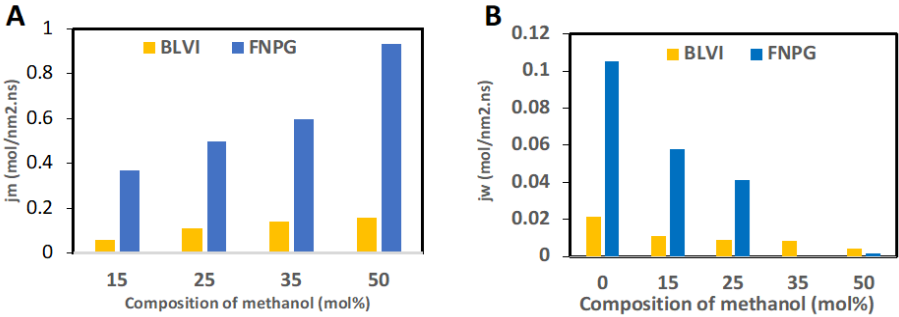


Fig 1. Evaporative fluxes of methanol (A) and water (B) with and without the presence of nanoporous graphene.

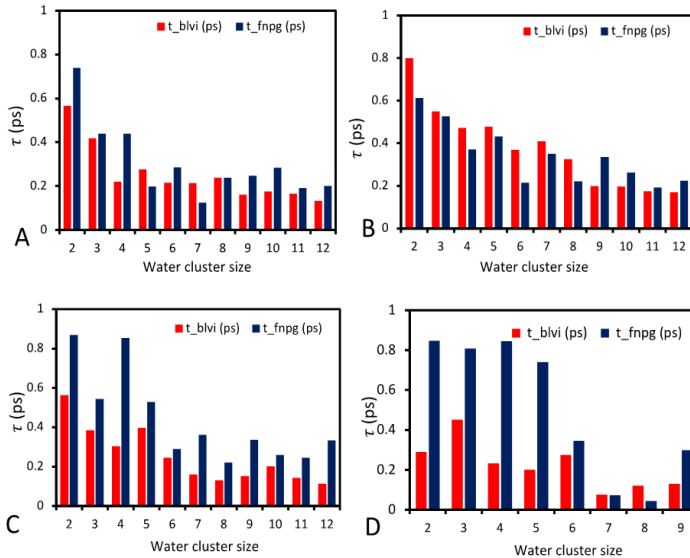


Fig 2: interfacial water cluster lifetimes for 15% (A), 25%(B), 35% (C) and 50% methanol (D) with and without the FNPG. BLVI stands for bare interface evaporation. Observe the longer survival times for water clusters beyond 35 % methanol.



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P1.8 WHIA: A Novel Cubic Equation of State for Accurate Modeling of Water Properties

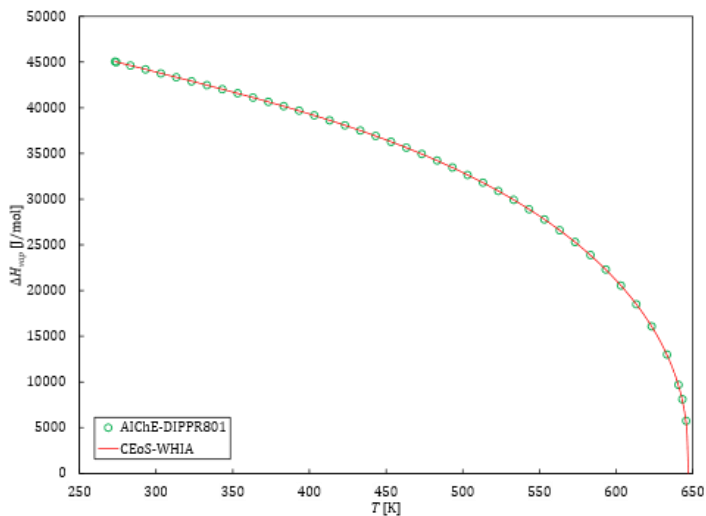
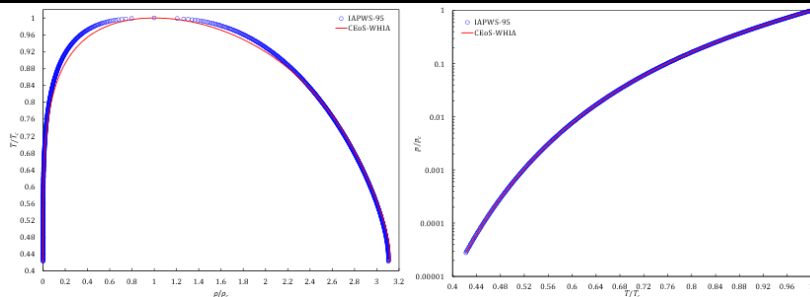
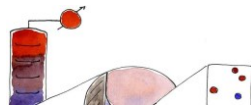
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This study proposes a corresponding state cubic equation of state (CEoS-WHIA) to address the limitations inherent in classical cubic, volume translation, and association extension methodologies for predicting the thermophysical properties of pure water. It focuses on calculating non-derivative properties, including entropy, enthalpy, internal energy, volume, and derivative properties, such as heat capacities, compressibilities, and the speed of sound. These properties of water were evaluated across various equations of state and compared against the IAPWS-95 [1], a specialized formulation for water, as well as experimental data from AIChE-DIPPR801 [2]. While all models yielded acceptable results for non-derivative properties, the association extension approaches encountered challenges in the near-critical region. Moreover, none of the methodologies effectively predicted the properties in supercooled and compressed liquid regions. Additionally, all approaches exhibited significant shortcomings in predicting derivative properties across all regions. The results indicate that CEoS-WHIA appropriately predicts thermodynamic properties in saturated liquid-vapor and superheated regions.



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P1.9 Engineering Protein Fibrils from Self-Assembly to Drug Delivery: Thermodynamic aspects

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Understanding misfolding and aggregation of proteins is important in disciplines of proteins, pharmaceutical, and biomedical fields. Protein misfolding and assembly results in formation of amyloid fibrils leading to crippling conditions referred to as "amyloidosis" [1,2]. They are fundamentally robust and insoluble nanofibres with considerable potential as nanotechnology and bionanotechnology materials. This work examines lysozyme fibrillation in the presence of pluronics (F68 and F127). In an A-B-A conformation, pluronic copolymers consist of three blocks: two hydrophilic poly(ethylene oxide) blocks (PEO, part A) and a hydrophobic poly(propylene oxide) block (PPO, part B). When pluronic copolymers are present in an aqueous solution, they self-assemble to form polymeric micelles, or micellar-type nanostructures, at concentrations higher than critical micellar concentration. Compared to micelles based on surfactants, these micelles are substantially more stable because they consist of a hydrophobic core and a hydrophilic surface [3,4]. A combination of calorimetry and spectroscopy has been used to obtain mechanistic insights into effect of pluronics on the protein aggregation/ fibrillation. Isothermal titration calorimetry results suggest that interaction of protein with F68 is exothermic while with F127 it is endothermic due to more hydrophobicity of the latter pluronic. The conformation of protein fibrils formation was examined by TEM images and ThT binding assay, which demonstrated that pluronics promoted fibrillation process rather than inhibiting it. The pre- and post-micellar concentrations of pluronics on interaction with protein (at varying fibrillation stages) exhibit a reduction in Δ value as the incubation time increases. This indicates formation of amorphous aggregates due to which endothermic enthalpy is observed. AGGRESCAN program was used to identify aggregation-prone regions of protein. According to analysis, pluronics interact with the areas that are not prone to aggregation, exposing hotspot areas to the solvent and triggering formation of fibrils. The knowledge of these fascinating macromolecular assemblies has been progressively expanding and deepening, from identifying the role of protein amyloid fibrils in neurodegenerative diseases to their



recent uses in high-performance materials [5]. Consequently, the potential use of these formed aggregates for drug delivery was explored. Interaction of anticancer drugs (5-fluorouracil and cytarabine) with the protein fibril systems was studied using calorimetry and spectroscopy. The results suggest one less order of binding for 5-fluorouracil with protein fibril systems than with cytarabine. Consecutively, static fluorescence quenching was observed in presence of these drugs. Moreover, cytotoxicity of the protein fibril system was examined with and without these anticancer drugs. UV-visible spectroscopy was used for adsorption studies. When cytarabine is used with protein fibrils, the hydrophobic interaction predominates, according to endothermic enthalpy of interaction, but the electrostatic interaction predominates with 5-fluorouracil. On the other hand, the former drug exhibited more adsorption on the surface of protein fibrils compared to the latter. Therefore, it is concluded that cytarabine has weak adsorption on fibril surfaces and is readily desorbed in cells, whereas 5-fluorouracil has relatively strong adsorption; as a result, the complex of LFF127 and 5-FU is fatal to malignant cells. These results are beneficial for exploring numerous applications of the formed protein fibrils/aggregates and in providing suitable strategies for the design and development of drug delivery agents.

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P1.10 Colloidal self-assemblies: Correlation of Structure-Property-Energetics Relationships in Drug Partitioning and Release

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Majority of synthetically developed new molecular entities or improved drug molecules have high hydrophobic content and low bioavailability. Therefore, suitable drug delivery vehicles are required for effective delivery of the drugs at the target site. Self-assembled hydrocolloidal structures such as surfactant micelles, niosomes, and liposomes offer an effective environment for drug encapsulation. Literature information on drug encapsulation in such self-assemblies has generally been qualitative in nature. We have quantitatively investigated the partitioning of a variety of drugs varying from antibiotic, anticancer, anti-inflammatory and antithyroid into self-assemblies of cationic, non-ionic and mixture of cationic and non-ionic surfactant micelles, as well as of niosomes and their interaction with the transport protein serum albumin upon subsequent delivery. Thermodynamic signatures accompanying the partitioning process [such as partitioning constant (K) and change in standard molar enthalpy (ΔH°), standard molar entropy (ΔS°), and standard molar free energy (ΔG°)] have enabled a quantitative understanding of the role of functional groups on the drug molecule and properties of the self-assemblies in encapsulation along with loci of partitioning. It is also observed that self-assemblies of non-ionic molecules allow partitioning of drug molecules in a sequential manner. Experiments on interactions of drug molecules upon release from such assemblies with the target protein have suggested that the binding process is not appreciably different than in that in the absence of self-assemblies. The effect of drug delivery vehicles on the thermal and structural stability of target protein (taken as transport protein bovine serum albumin and human serum albumin) have been investigated quantitatively. The results have been correlated with different class of drugs of different nature to understand the role of molecular features in the partitioning process. These studies have significance in understanding the physical chemistry underlying partitioning of a variety of drug molecules into suitable delivery vehicles and permit establishing structure-



property-energetics relationships.¹⁻⁴ Such studies provide general guidelines towards a broader goal of rational drug design.

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P1.11 Adsorption of cryogenic hydrogen into carbon-based materials through Grand Canonical Monte Carlo simulations

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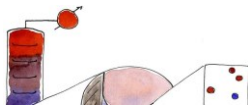
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A solution to reduce the impact in the environment due to the greenhouse gases is employing hydrogen as an energy source. It is important to have a method to store this hydrogen, where several methods are available. Among the options, adsorption into solid materials is a method that is reliable and can reduce the volume of the stored hydrogen.

Over the years, different materials have been tested to see their capacity to adsorb hydrogen and facilitate a reversible process. From the materials available, carbon is known for its high adsorption capability for several gases, presenting different morphologies with highly porous structure [1]. In general, activated carbon, carbon nanotubes and graphene sheets are considered good alternatives due to their high surface area to maximise the adsorption process. The light weight and reversible gas adsorption/desorption characteristics make carbon-based materials an ideal candidate to be employed for hydrogen storage. These materials have been studied through the last century in order to understand the mechanisms of adsorption and to test variations to increase their sorption capacity. However, there are theoretical studies in literature predicting high storage capacities in materials that cannot be confirmed experimentally [2]. The lack of accurate theoretical models to take into account pore distribution and realistic pore shapes, and the cost and difficulty of experimental trials, make molecular simulations a well established method to investigate different structures and morphologies.

Here we carry out Monte Carlo simulations in the Grand Canonical ensemble to study the confinement in several carbon-based materials of hydrogen at both cryogenic (77K) and room temperature (298K). The adsorption isotherms produced from the adsorption of hydrogen into the different solid materials are compared against each other in the range of pressure between 0 and 60 bar. Among the structures studied we can mention; carbon nanotubes, graphene slit-like pores, corrugated graphene slit-like pores, graphene-slit like pores, graphene nanoflakes amorphous material, graphene nanoflakes amorphous material, amorphous



materials built from platonic hydrocarbons (tetrahedrane, cubane, dodecahedrane), and fullerene-based materials. Selected preliminary results are displayed in Fig. 1.

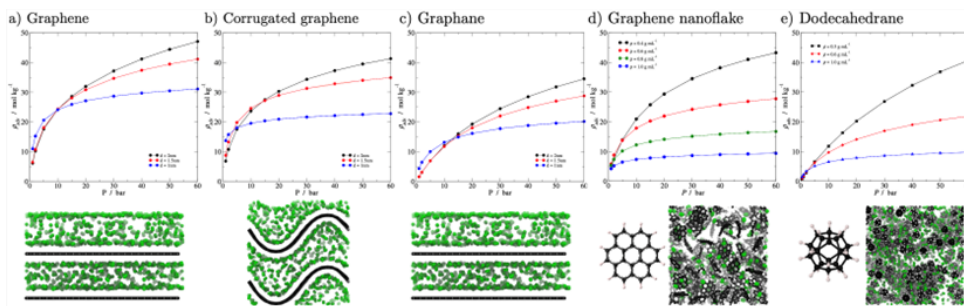


Fig. 1. Adsorption of hydrogen at 77K in different carbonaceous materials; (a) graphene slit-like pore, (b) corrugated graphene slit-like pore, (c) graphane slit-like pore, (d) amorphous graphene nanoflakes, and (e) amorphous dodecahedranes.

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P1.12 How the enthalpy, free Gibbs energy and entropy affect the treatment of wastewaters: The case of the removal of Cr(VI) by chitosan/curcumin/activated carbon adsorbent

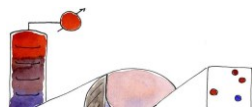
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Various anthropogenic activities, such as industrial and mining processes, lead to the contamination of natural water bodies with noxious heavy metal ions by discharging untreated or partially-treated effluents into the environment. Hexavalent chromium poses a serious threat to the environment and public health due to its toxic effects on humans, animals, plants and microorganisms and is regarded as a priority pollutant in many countries [1, 2], while it is classified by the International Agency for Research on Cancer (IARC) as a group I human carcinogen [3]. Hence, the employment of effective Cr(VI) removal methods on various wastewater effluents is deemed necessary. Among the various methods for heavy metal ion removal from aqueous media adsorption is the most suitable due to its high efficiency, inexpensiveness, operational simplicity and up-scalability [4, 5]. The overall process is governed by the interactions between the pollutant molecules and the adsorbent's functional groups. Therefore, the thermodynamic parameters enthalpy, free Gibbs energy and entropy of the adsorbate–adsorbent system provide helpful information on the process and sorption mechanism [6].

In this study, a novel green composite material, namely chitosan/curcumin/activated carbon adsorbent, was employed for the removal of Cr(VI) from aqueous solutions. Activated carbon is the most popular adsorbent material due to its vast surface area and porosity. Nevertheless, since it is mostly nonpolar, it reduces the attraction of cationic metal compounds to its surface and displays poor adsorption efficiency. For this reason, it is often combined with other materials to improve its effectiveness. Curcumin is a natural polyphenolic substance derived from the plant *Curcuma longa*. Previous research has shown that encapsulating curcumin in nanoparticles improves its capacity to absorb metal ions [7]. Chitosan, as a biopolymer, is inexpensive and possesses intriguing adsorption capabilities due to the presence of amino and hydroxyl groups along its macromolecular chains [8].



Their adsorptive efficiency towards Cr(VI), was evaluated by batch adsorption experiments. The effect of the pH value, contact time, adsorbent's dosage and initial chromium concentration was initially examined in order to choose the optimum conditions of the process. Adsorption isotherm data were fitted to the Langmuir and Freundlich models and were used to calculate the thermodynamic parameters at different temperatures. The spontaneous nature of the adsorption of Cr(VI) on the adsorbent was confirmed. Overall, the results indicate that this green material can be effectively employed for removal of hexavalent chromium from aqueous solutions.

Acknowledgements

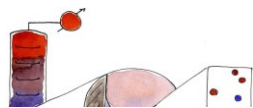
We acknowledge support of this work by the project “Advanced Nanostructured Materials for Sustainable Growth: Green Energy Production/Storage, Energy Saving and Environmental Remediation” (TAEDR-0535821) which is implemented under the action “Flagship actions in interdisciplinary scientific fields with a special focus on the productive fabric” (ID 16618), Greece 2.0 – National Recovery and Resilience Fund and funded by European Union NextGenerationEU.

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P1.13 Unravelling the effect of molecular interactions on macroscale properties in Sustainion and Poly ether ether ketone (PEEK) anion exchange membranes (AEMs) under hydrated conditions using MD simulations

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Considerable research is being pursued to alleviate the issues in anion exchange membranes (AEMs) in order to make these novel polyelectrolytes comparable in performance to proton exchange membranes, the current industry standard for fuel cells and water electrolyzers. Although there are several advantages of using AEMs, these materials suffer from very low conductivities of the anions which hamper their usage in large industrial setups needing considerable power densities in the equipment. The bottom-up approach of designing membranes based on microscopic properties has gained traction amongst many researchers primarily because such methods have very good predictability and excellent transferability between different properties. In this work, we have performed molecular dynamics simulations to determine the thermodynamic and transport characteristics, namely the density of the membranes and the diffusivity and conductivity of the anions for both Sustainion and Poly ether ether ketone (PEEK) anion exchange membrane. These membranes have given quite a credible performance as AEMs in a water electrolyser, but the atomistic details of these materials are yet to be studied. Our work aims at bridging this critical gap in literature by providing a detailed molecular understanding of the behaviour of the Sustainion and PEEK AEMs under different levels of hydration at different temperatures. The density exhibits a non-monotonic trend while the diffusivity showcases a non-linear behaviour with hydration, similar to what has been observed for other membranes. Furthermore, the dependence of temperature on diffusion is Arrhenius-like with the activation energies exhibiting a non-monotonic relationship akin to the density. An



explanation for these different phenomena is provided on the basis of the counteracting influence of the potential of mean force and co-ordination number of the ions at different hydration levels. Finally, the simulation results are compared with experimental data, further underscoring the relevance and robustness of our molecular model.^{1,2}

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P1.14 Greenhouse Gas Capture using Molecular Simulation from Surfactant-Modified Solid Surfaces

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Nowadays, the emission of greenhouse gases have caused major climate changes, which has generated great scientific and technological interest in the remediation of this problem[1,2].

One solution to this is the capture and storage of gases, such as carbon dioxide, CO_2 , methane CH_4 , and nitrous oxide, N_2O , through the adsorption of gases in porous media using inorganic materials such as zeolites and silicas, and organic materials, such as MOFS and carbons[3-5]. In this sense, the efficiency of gas retention can be determined by the characteristics of the solid, such as pore size, surface specific area or geometry[6]. Although the aim is to improve retention efficiency, the synthesis of new materials with better characteristics can be expensive. Therefore, it is necessary to explore other alternatives to improve efficiency in the capture of greenhouse gases.

During recent years, innovative methods have been developed that use different types of surfactants for the capture and storage of CO_2 [7-12]. These compounds have the ability to facilitate gas diffusion and transfer, which makes them a promising option to improve the efficiency of traditional adsorbents. BET surface area, SEM images, porosity and porous area measurements showed that adsorption capacity of cadmium on carbons can be significantly enhanced by modification with surfactants [13].

In this work we explained from the atomic-molecular point of view the adsorption of CO_2 and CH_4 on two solid surfaces, asphaltene-slit and graphite-slit, when three types of surfactant molecules are present: cationic, dodecyltrimethylammonium bromide (DTAB), anionic, sodium dodecyl sulfate (SDS), or amphoteric, betaine, through molecular simulation. We determined what are the relevant interactions between the polar and non-polar groups of amphiphilic molecules with gases to establish the mechanism of the formation of new molecular aggregates on solid surfaces.



In general, the simulations reveal that the presence of surfactants leads to enhanced gas adsorption, even doubling the adsorption capacity. Density profiles illustrate the formation of bilayer structures of surfactants on the surfaces, creating additional adsorption sites for gases. The pair correlation functions elucidate the arrangement of gas molecules around surfactants, highlighting the preferential interaction of CO₂ with surfactant headgroups. Overall, our findings underscore the potential of surfactant-modified surfaces for improved greenhouse gas capture, offering insights into the underlying molecular mechanisms governing gas adsorption behaviour.

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P1.15 Inverted Classroom Concept applied to a Chemical Thermodynamics Exercise

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The Technology Enhanced Learning (TEL) Marketplace is a joint initiative by the vice rectorate for academic affairs and the vice rectorate for digitalisation and change management at TU Graz to modernize lectures. In the course of this initiative, a Chemical Thermodynamics exercise that is part of one bachelor program (Chemical & Process Engineering) and two master programs (Biorefinery Engineering and Chemical & Pharmaceutical Engineering) was transformed into the inverted classroom format. [1]

The core of this concept are interactive notebooks created in Wolfram Mathematica for each individual calculation example. With these notebooks, students can work through the examples independently, in-depth and irrespective of time, with the required theoretical background integrated into the notebooks. [2] In contrast to conventional teaching, the interactive part of the course does not involve calculating the examples in detail, but rather discussing the tactical approaches, solutions and problems that arose during the calculations, which raises the overall level of content teaching.

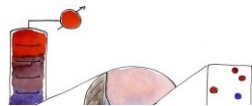
This contribution reports on the workflow of the transformation process from ex-cathedra teaching to the inverted classroom concept, the setup of the exercise, the innovative teaching materials used, the experiences with this concept from the point of view of teachers and students and presents results from a questionnaire-based evaluation of the notebooks and the new course design after two semesters.

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P1.16 Apparent molar volumes of industrially relevant solutes in CO₂ near the critical point

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CO₂ is an appealing solvent in industrial applications due to its non-flammable, non-toxic nature. It can be considered a green solvent if it is not emitted as waste and reused in industrial processes as it directly contributes to carbon utilization. CO₂ can be used in the selective extraction of solutes from bulk plant matter, such as caffeine from coffee beans and terpenes from plant waste [1]. Aliphatic alcohols are often used as a cosolvent in CO₂ to increase the solvating power towards more polar solutes [2]. To this end, it is beneficial to understand the thermodynamic properties of dilute CO₂ solutions and to accurately calculate solution properties. This is especially important near the critical point of the mixture as high compressibilities result in large changes for thermodynamic and volumetric properties at these conditions; furthermore, there are a lack of experimental data. In this work we present measured apparent molar volumes of various solutes including aliphatic alcohols, terpenes, caffeine and cannabidiol in CO₂ from binary solutions. A flowing vibrating tube densimeter upgraded for high pressure is used to collect the experimental data. This data is used to correlate the properties of binary CO₂ solutions using reduced Helmholtz equations of state [3-5] and fluctuation solution theory (FST) [6]. Figure 1 shows the measured apparent molar volumes of methanol in CO₂ at 308.0 K as a function of pressure as well as the calculated apparent molar volumes using the reduced Helmholtz and FST equations of state.



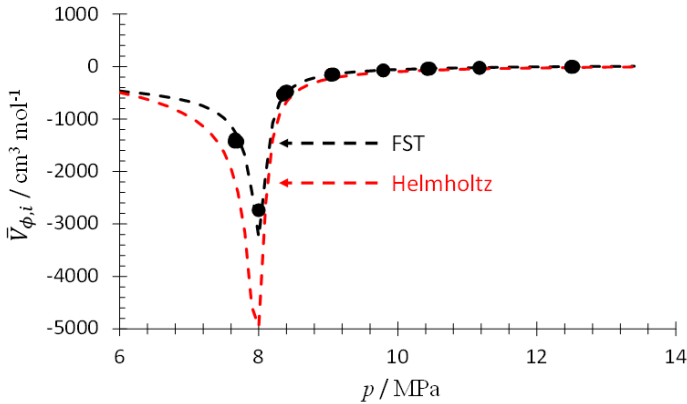


Figure 1. Measured apparent molar volumes of methanol in CO_2 at 308.0 K as a function of pressure (●) compared to the fits obtained using the reduced Helmholtz (---) and FST (---) equations of state.

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P1.17 Thermodynamic properties of hazardous gas mixtures in the context of CCUS by combining Raman spectroscopy and a predictive cubic EoS

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In the effort to limit climate change, there has been a significant emphasis in recent years on developing effective methods for carbon capture, utilization, and storage (CCUS)[1]. Depending on the gas stream sources and the employed capture technology, the CO₂ stream could contain other co-captured gases, such as N₂, O₂, SO_x, Ar, NO_x, or CH₄. The presence of these contaminants could impact the design and operation of CCUS [2]. If some gases like Ar or N₂ can dominate the composition of impurities, other gases such as NO_x or SO_x can be minor. Still, they may cause the system to be chemically reactive or modify the physical properties of the gas mixture (phase equilibria, viscosity, etc.). Therefore, the primary goal of this study is to provide new data on the thermodynamic properties of CO₂-rich gas mixtures. In this research, new VLE data for two binary systems, namely CO₂+NO and SO₂+NO, are obtained by acquiring Raman spectra of various gas mixtures confined in silica micro-capillaries [3] within ranges of operational pressure and temperature conditions that are applicable for CCUS purposes. However, Raman spectroscopy requires calibration to provide quantitative data. More precisely, the composition of a gas mixture can be obtained from the Raman spectra using Relative Raman Scattering Cross Sections (RRSCS)[4]. As the literature values for RRSCS are dated and with unknown uncertainty, the RRSCS of NO and SO₂ are re-evaluated in this work considering the Raman peak area ratio to N₂ (Fig. 1). In order to consolidate the VLE knowledge of these systems, VLE data are then obtained by combining optical observation in micro-capillary and Raman spectra in the different phases as a function of temperature and pressure. These Raman data are finally compared to the results of two different thermodynamic models, namely



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the Enhanced Predictive Peng-Robinson (E-PPR78 model) and the Peng-Robinson EoS with an advanced class of mixing rules [5,6].

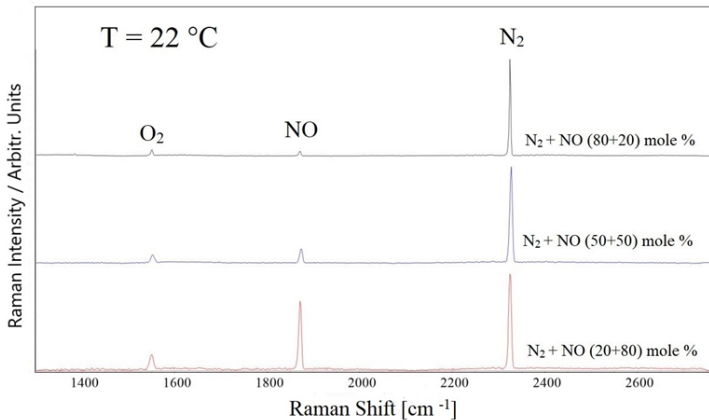
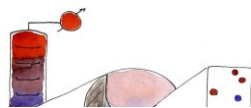


Fig. 1. Raman spectra for NO+N₂ at different compositions

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P1.18 Metastable States of a Model Substance

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We have recently introduced [1] an Ising-like model allowing every aspect of the phase diagram of a simple substance like argon to be reproduced (see Fig. 1). The thermodynamic description of the model's metastable states $\frac{3}{4}$ feasible at a mean-field level [2] $\frac{3}{4}$ is the subject of the present communication. Attention shall be mostly devoted to spinodal loci, as the mean-field limit of the regions of the phase diagram where solid, liquid, and gas phases can exist. It is found that each metastable two-phase equilibrium line ends at a point in a spinodal recently referred to as “Speedy point” [3]. Furthermore, the expedience of suppressing the liquid spinodal naturally opens the way to a metastable liquid-liquid transition such as the one proved for models of water [4]. Lines along which our simple-substance model might be extended to water shall be depicted.

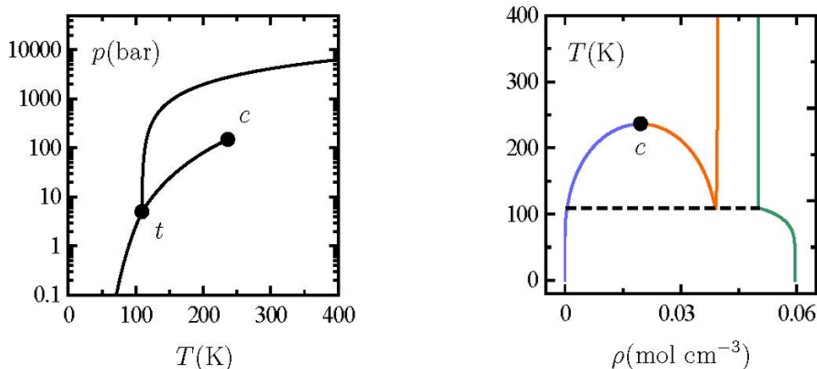
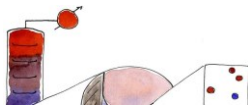


Fig. 1. Phase diagram for the simple-substance model in the p - T and T - ρ planes. Lines in the p - T plane determine the conditions of two-phase coexistence bounded by the triple point t and the gas-liquid critical point c . Lines in the T - ρ plane enclose regions of two-phase coexistence for crystal (green), liquid (orange), and gas (blue), with horizontal dashed lines joining the states of three-phase coexistence associated with t .



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P1.19 Shape Anisotropy Effects on Tetratic Ordering of Quasi-1D Hard Superdisks

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This study investigates the orientational characteristics of a quasi-1D system of hard superdisks, where the centers of the particles are allowed to move on a straight line, but they can freely rotate in the embedding 2D plane. By varying the deformation parameter of the superdisk, it is possible to tune the shape of the particle between a disk and a square. For the computation of equilibrium properties, we use both a theoretical approach (transfer matrix method) and extensive simulations in the NVT and NPT ensemble, with a special focus on the effects of the superdisk deformation parameter on the orientational properties. We found that the superdisks form a tetratic phase except in the hard disk limit, where the symmetry of the particle changes from fourfold to continuous. Therefore, the phase behavior of hard disks is identical to that of 1D hard rods, while the superdisks behave similarly to hard squares. Interestingly we found that the orientational correlation length exhibits a power law divergence as a function of pressure with exponent ranging between 0 and 1/2 as the deformation parameter is increased from 2 (disks) to infinity (squares). This finding indicates that orientational jamming is weakened as the shape is tuned from square to disk. Furthermore, the respective exponents for the angular fluctuations and the equation of state are discontinuous when the shape changes from disk to superdisk (symmetry breaking point).

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P1.20 Mechanistic details of the organizer assisted nucleation of gold nanoparticles by Turkevich method

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Gold nanoparticles (AuNPs) are one of the most widely used and studied nanomaterials with potential applications in nano-medicine, bio-nanotechnology, microelectronics, optics, and catalysis. Precise control of these nanoparticles' size, shape, and synthesis protocols is important in tuning the material properties at bulk. Turkevich method for synthesizing citrate-stabilized AuNPs is the most popular method because of its straightforward methodology and reliability in producing highly stabilized AuNPs ranging from 5 to 150 nm. The mechanism involves the reduction of auric Au^{3+} species to aurous Au^+ species using trisodium citrate, and disproportionation of the aurous Au^+ species to metallic gold (Au) atoms. Several studies have been conducted in the last 20 years to understand the mechanism of the Turkevich method. It has been hypothesized that the disproportionation of aurous Au^+ species is aided by the formation of a complex between aurous Au^+ species and di-carboxy acetone (DCA) which is a by-product of the first reaction involving reduction of auric Au^{3+} species. However, there has been no direct evidence through experiments or molecular simulation on the existence of such a complex. In this work, we use molecular simulations to study the nucleation of AuNPs from the aurous Au^+ species with specific focus on the role of DCA as an organizer. The simulations are able to give detailed insights into the mechanism of AuNPs formation including the structure of the complex between Au^+ and DCA. The simulations reveal a probable two-step nucleation mechanism consisting of (i) nucleation of the DCA- Au^+ complex into a cluster and (ii) nucleation of metallic gold within this cluster. The nucleation mechanism proposed in this work can serve as a prototype in other organizer assisted nucleation of metallic nanoparticles.

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P1.21 Computing solubility and thermodynamic properties of reactive oxygen and nitrogen species in water

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Non-thermal plasmas are ionized gases which are not in thermal equilibrium as the average electron energy (~ 10 eV) is higher than the average energy of heavy particles (~ 0.025 eV) in the gas. Air plasmas are rich sources of reactive oxygen and nitrogen species (RONS) such as H_2O_2 , NO, NO_2 , OH, O. Owing to their capability of producing RONS without creating significant thermal damage, they find applications in biomedicine, material processing, agriculture and soil/water remediation. In all these applications, interaction of RONS with a liquid medium (e.g., water) plays a crucial role as these interactions affect the uptake of RONS by the liquid and, consequently, impact the efficacy of plasmas for these applications [1]. Our goal is to systematically investigate the thermodynamic properties of the interaction of RONS with liquid water using molecular simulations (i.e., Continuous Fractional Component Monte Carlo simulations and Molecular Dynamics). As a step towards our goal, we have investigated the behaviour of hydrogen peroxide and nitric oxide in water. An integral part of the molecular simulations is the force field parameters that should be verified and validated before making any predictions. For H_2O_2 , the quality of two H_2O_2 force fields (Orabi [2] and Cordeiro [3]) and four water force fields (TIP3P, mTIP3P, TIP4P/2005, TIP5P-E) were analysed. The TIP4P/2005 force field in combination with both the H_2O_2 force fields were able to capture the thermodynamic properties of H_2O_2 aqueous solutions in agreement with the experiments. The solubility of H_2O_2 in water was better predicted by the Cordeiro force field for H_2O_2 in combination with the TIP3P and mTIP3P force fields. For NO, we developed new force field parameters that take dimerization of NO at low temperatures (upto 180 K) into account. Our force field is able to reproduce the vapor-liquid equilibrium properties such as coexistence densities, critical temperature and density, and



saturation vapor pressures in reasonably good agreement with experiments. In addition, our force field can predict the heat of vaporization of NO in good agreement with the experiments. Our results can be used by macroscopic plasma fluid models to determine the uptake of H₂O₂ and NO in water.

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P1.22 A mystery resolved? Towards a working mechanism behind nonphotochemical laser-induced nucleation

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Crystallization from solution is central to technological applications ranging from nanomaterial synthesis to pharmaceutical manufacturing [1]. Among the strategies proposed to control kinetics and emerging crystal properties, nonphotochemical laser-induced nucleation (NPLIN), where one or more unfocused laser pulses trigger accelerated nucleation in supersaturated solutions, emerged as a promising approach due to its presumed nonchemical nature and ability to influence polymorphic form. Several putative mechanistic hypotheses, ranging from molecular phenomena relying on (an)isotropic polarization and isotropic electronic polarizability of solute clusters to microscale phenomena based on impurity heating and consequent cavitation, have been proposed in an attempt to explain the observations. However, the exact mechanism behind NPLIN remains elusive[2]. We demonstrate that a cavitation bubble initiated by a Nd: YAG laser pulse below breakdown threshold induces crystallization from supersaturated aqueous solutions with supersaturation and laser-energy-dependent nucleation kinetics. Combining high-speed video microscopy and simulations, we argue that a competition between the dissipation of absorbed laser energy as latent and sensible heat dictates the solvent evaporation rate and creates a momentary supersaturation peak at the vapor-liquid interface. The number and morphology of crystals correlate to the characteristics of the simulated supersaturation peak. The findings provide a significant step towards pinpointing the underlying mechanism behind NPLIN. Moreover, they contribute to the interdisciplinary field of nucleation control of crystallization from solution with applications ranging from resource recovery for circularity to desalination.

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P1.23 Contaminant desorption from a dolomite plate with synthetic and biosurfactant molecules: A Molecular Dynamics study

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Using the molecular dynamics methodology, we study the desorption of contaminants on a dolomite plate using surfactants. This work used two surfactants to compare their capacity to desorb hydrocarbons deposited on the solid surface: a synthetic surfactant, sodium dodecyl sulfate (SDS), and a biosurfactant called surfactin. Additionally, a mixture of both surfactants was prepared at different proportions to find an optimal concentration.

The results show that the mixture presents the better desorption of the contaminants from the dolomite surface. Furthermore, we explore the impact of an electric field on the desorption process.



P1.24 Improved TPT and molecular dynamics simulations of square-well fluid mixtures and trimers of various conformations

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The theoretical development of statistical and thermodynamical tools to deal with fluid mixtures has witnessed an extraordinary success in dealing with quite a wide range of complex systems, including many of industrial interest [1,2]. This success has been possible due to the use of sophisticated and flexible interatomic potentials such as that used in the SAFT- γ Mie approach, although in its earlier stages the SAFT-VR theory relied in the simpler and more basic square-well, SW, interaction [3,4]. Due to its simplicity and to the fact that it is perhaps the simplest system to exhibit a vapour-liquid coexistence, the SW fluid has continued to attract the interest of researchers [5,6,7]. Recently, our group has developed theoretical and simulation tools to study simple and complex systems of models based on the SW interaction [8-11]. During such a study, among many other interesting findings, we made explicit inadequacies of the current Thermodynamic Perturbation Theory, TPT-1, in treating even the simplest systems such as SW dimers and trimers. In particular, the theoretical treatment of the SW dimer, in spite of a respectable history of inquiry [12], showed unexplained deviations –when compared with simulations– in the shape of the vapour-liquid coexistence curve near the critical point. The obstacle was removed by using an improved SW free-energy equation and developing new correlations, valid for a range of values of the SW range λ , for the SW radial distribution at contact, $g_{sw}(\sigma)$, a crucial element in the SW TPT-1 treatment [13]. This improvement allowed to extent the approach to deal with various SW trimers, including those with a SW atom replaced by a hard-sphere, HS, [14]. The results for the full SW-SW-SW trimer agreed very well with simulations [10]. Nevertheless, the case of the trimers with a HS replacement showed gross inadequacies of the theory. In this work we introduce an improved TPT theory to deal with this type of systems.

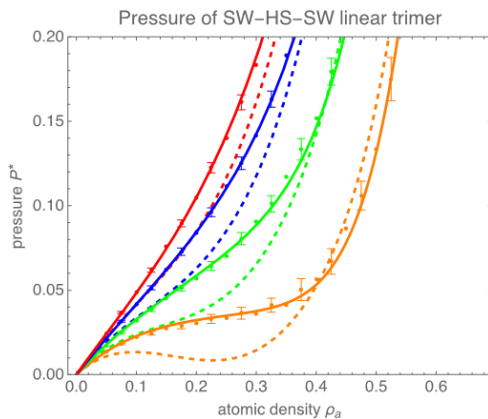
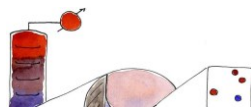


Fig. 1. shows pressure isotherms at $T^* = 0.99$ (orange), 1.17 (green), 1.35 (blue) and 1.5 (red) of the SW-HS-SW linear trimer compared with our MD results. TPT-1 + linear approximation: dashed lines. Improved theory including $g_{sw}(\lambda)$: solid lines.

Improved TPT theories for chain or ring molecules consist of two main components, all at the level of the fluid's free energy: 1) An equation for the monomer or atomic fluid, which for the system of interest consists of a HS+SW mixture, and 2) the chain term, containing for trimers the cavity function $y(1,2,3)$ at the appropriate configuration of the particles (1,2,3). The absence of reliable means to calculate accurately the function $y(1,2,3)$ leads to the wide use of the so-called linear approximation, LA, setting $y(1,2,3) = y(1,2) y(2,3)$. This implies the need of an extra third –or tail– term.

We propose here a new equation for the free energy of the HS+SW mixture built on a 4th-order high-temperature expansion, HTE. We also present new molecular dynamics simulations of the same fluid mixture and of four different trimers, used to test the theory. The composition dependence of the model is inspired in the van der Waals 1-fluid approach used successfully for SW fluids by Vidales et al. [15] and Galindo *et al.* [4]. To obtain a self-consistent theory, the values of $g_{sw}(\sigma)$ and $g_{sw}(\lambda)$, are obtained by an old SW algorithm [16]. Nevertheless, the theoretical predictions still deviated from simulations. Introduction of high-order terms that improve the LA and referred to generically as TPT-2 proved insufficient [17-18]. It was necessary to introduce a semi-empirical correction to TPT-1 involving $g_{sw}(\lambda)$, which is a novel feature. The final agreement between theory and simulation is excellent.



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P1.25 Dispersion Properties of Refractive Mixing Rules for Gaseous Mixtures

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The characterization of gaseous mixtures is an increasingly important issue in the fields of fuel analysis and aerosol research. Analyses by refractometry combined with refractive mixing rules are also powerful tools in this area. In this work, a three-laser interferometer and a vacuum system were projected and constructed to measure the refractivity of pure inert gases like N₂, CO₂, Ar, and O₂ and to study mixtures with those gases. The light sources used in the experiments were a He-Ne laser (632.8 nm), a frequency-doubled diode-pumped Nd:YAG laser (532 nm), and a red diode laser (653 nm). The experimental refractivity data of binary mixtures of N₂ and Ar as a function of the molar fractions of the gases for the three wavelengths were compared with the theoretical ones obtained from a modified, temperature invariant, Gladstone-Dale based refractive mixing rule by introducing the parameter thermal refractivity. The results obtained by the modified refractive mixing rule proposed for dry air were also compared with the refractive measurements of atmospheric air for the three wavelengths. In general, the experimental results have shown good agreement with the theoretical predictions, and the dispersive character of the thermal refractivities point out to promising applications in evaluating gas mixtures.

Acknowledgement

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P1.26 Measurements and Theoretical Modelling of Isobaric Vapor-Liquid Equilibria and Dynamic Viscosity for the Dibutyl Ether and n-Butanol Binary Mixture

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Mixtures of ethers and alcohols have played a pivotal role in the formulation of oxygenated additives for gasoline. This has led to some studies focused on its structural effects and its environmental impact, which account for their ability to improve the octane number and reduce engine emissions [1, 2]. Although environmental studies are of utmost importance in this new paradigm of chemical engineering, it is always mandatory to complement them with methodologies that describe the molecular behaviour of any system of interest. Different combinations of ethers (linear and cyclic molecules) and low molecular alcohols have been experimentally measured and characterized in the literature, with vapor-liquid equilibrium (VLE) being one of the most valued physical properties; nonetheless, most of these works are not based on molecular approaches. Some avant-garde contributions are highlighted, although they explore other types of oxygenated additives like esters [3]. On the other hand, it seems that dynamic viscosity has not received much attention, even though this transport property is vital in the design of engines and transport equipment [4]. Subsequently, a methodical approach for characterizing these oxygenated blends is still needed.

In the case of the dibutyl ether and n-butanol system, there is only the work of Lladosa et al. [5] regarding the calculation of its VLE based on macroscopic models at low and atmospheric pressure. This motivates us to present new and consistent experimental data measured in different conditions, which are also feasible in its exploration. This joins our goal to assess the predictive power of some state-of-the-art molecular models. In the case of an ether/alcohol mixture, induced association and polar effects are substantial chemical phenomena to consider in their modelling, which are explicitly described by SAFT models.

In this work, we propose a formalism for characterizing the dibutyl ether and n-butanol binary mixture in terms of its VLE and dynamic viscosity. The VLE is measured at three isobaric conditions (50.00, 75.00, and 94.00 kPa), and its dynamic viscosity is quantified at 298.15 K and atmospheric pressure within the



whole range of composition. A full-predictive scheme based on the SAFT-VR Mie equation of state with polar contributions [6, 7] is applied to predict both properties. In the case of the transport property, the equation of state is first incorporated in a modified scaling theory for the Helmholtz energy [8]. Preliminary results displayed in Fig. 1 reveal the azeotropic behaviour of this mixture with positive deviation from the ideal solution model as well as the negative departure from the linear trend of its dynamic viscosity. SAFT-VR Mie can predict both physical properties with acceptable accuracy, although some deviation is evident in the vicinity of the azeotropic point.

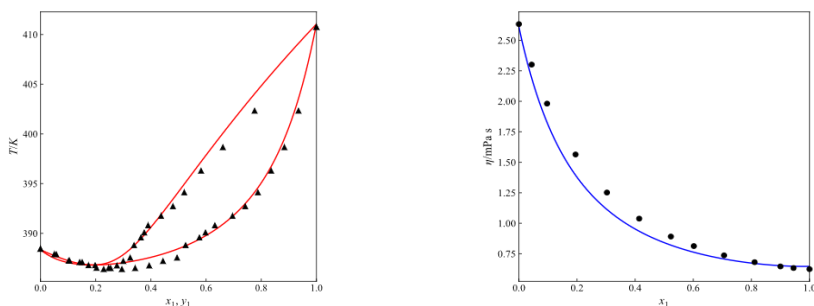


Fig. 1. Characterization of the dibutyl ether (1) and n-butanol (2) binary mixture. (a) VLE at 94.00 kPa: experimental data (●) and predictions from the SAFT-VR Mie equation (—). (b) Dynamic viscosity at 298.15 K and 101.3 kPa: experimental data (●), and predictions from the Helmholtz scaling theory with the SAFT-VR Mie equation (—).

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P1.27 A New Class of Descriptors for Nanoporous Materials and its Applications to Classification and CO₂ Gas Adsorption into zeolites

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The generalization of the high-throughput synthesis has recently allowed the discovery of thousands of new porous materials generating a large amount of information with the development of specialized databases. Widespread access to databases enabled the increase of algorithms and models for property prediction and in-silico design of materials. The structural information of materials still needs to be rationalized by the inclusion of descriptors to ease the characterization of solids [1,2]. This is essential for in-silico screening to potential applications based on Machine Learning (ML) approaches. Indeed, at the forefront of a real revolution in the selection and design of porous materials for many industrial applications, the use of appropriate descriptors to encode solid material properties (topology, porosity, surface chemistry) is one of the fundamental aspects of the development of ML-based models. Our analysis of the literature reveals a lack of descriptors based on the Potential Energy Surface (PES) of crystalline materials embedding crucial information such as the porosity, the topology, and the surface chemistry [3].

In this work, we introduce new PES-based descriptors including the surface probability distribution of the local pore curvature (KH), the electrostatic-potential energy surface distribution (s_e), as well as the local electrostatic-potential gradient surface probability distribution ($\tilde{N}s_e$). Descriptors proposed in this work can be considered as signal signatures of the solids that must be processed using data binning by subsampling distribution functions before being used as input for ML techniques.

We exploited this fact by performing a deeper classification of the pure siliceous zeolite structures available in the IZA database by means of Principal Component Analysis (PCA) of the three descriptors as can be seen in Figure 1.a,



as well as its characterization by self-containing standard morphological and topological information (pore diameter, tortuosity, surface chemistry, etc.). We illustrate their usage to generate accurate ML-based models of isosteric heat of adsorption of CO₂ on purely siliceous zeolites of the IZA database (Fig 1.b). We have identified the values of the maximum pics of the (s_c) distribution with the main adsorption sites and configurations of CO₂ adsorbed molecules over the accessible surface of LTA Na-ion exchanged zeolites at different Si/Al ratios as shown in Fig.1.c. This important information has been used to define as new numerical fingerprint (descriptor) for the prediction of the isosteric heat of adsorption of CO₂ molecules on Na⁺ ion-exchanged LTA structures with different Si/Al ratio as shown in Fig 1.d. The generality of the proposed descriptors allows a straightforward transferability to any type of porous material (MOFs, among others) without any restriction on the possible chemistry of the system (i.e., a reasonable force field/point charges capable of describing the interaction energy of the probe particle with the atoms of the framework) [4].

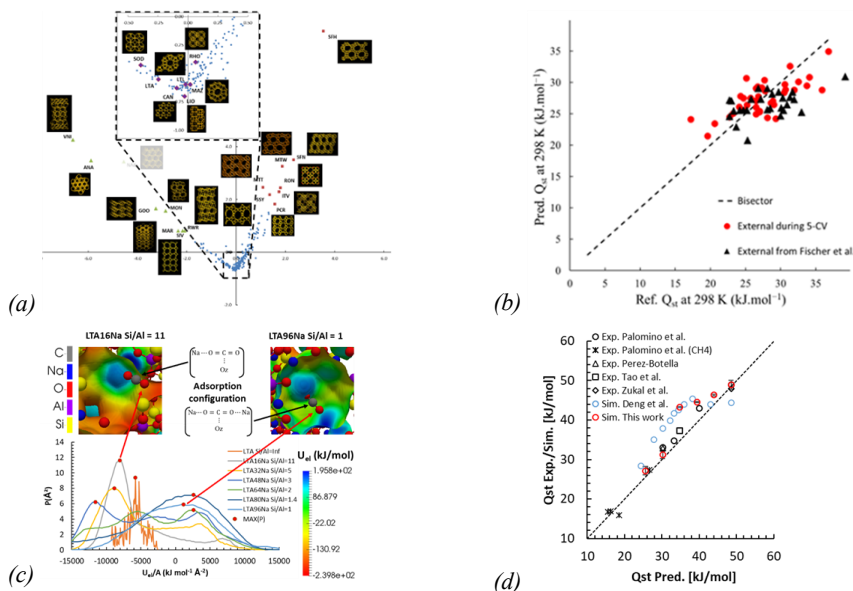


Fig 1. a) V-Shape classification map of the International Zeolite Assoc. (IZA) database. b) Parity plot of isosteric heat of adsorption of CO₂ on purely siliceous zeolites from the IZA database predicted using Support Vector Machine (SVM) and our descriptors. c) Variation of the electrostatic potential probability distribution-se of ion-exchanged LTA structures at different Si/Al ratios where the red dot represents the maximum of the distribution (MAX(P)) which are related to the (highlighted by the red arrows) CO₂ adsorption configurations (L-shape and T-

$$A = -kT \ln Q$$



shape highlighted by the black arrows) over the accessible surface area protected by the electrostatic energy as shown by the images at the top, representing two solids with Si/Al of 11 and 1 respectively. d) Parity plot representing the prediction of our descriptors for the Q_{st} for CO_2 and CH_4 respectively. Comparison of different experimental data for CO_2 and CH_4 and simulation results from the literature with our own MC simulations results for CO_2 .

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P1.28 Enthalpy of Dissociation of CO₂ Hydrates along the Three-Phase Equilibrium Line

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Under appropriate conditions of high pressure and/or low temperature, water molecules can self-organize in forming 3-dimensional crystalline structures, containing cages/cavities that can be stabilized by the presence of molecules that can fit within the cages (e.g. methane, carbon dioxide, nitrogen, ethane, etc.). Such ice-like, non-stoichiometric materials are known as clathrate hydrates or simply hydrates [1]. Hydrates are encountered in a variety of applications of industrial interest covering areas of energy- or environmental-related issues. Typical examples where hydrate formation/dissociation can occur (or can be of practical use) include flow assurance in oil/gas industries, gas storage/transportation, gas mixture separation, water desalination, climatic change, future energy sources, etc.

Among the thermodynamic properties of interest during the design stages of hydrate-related processes is the enthalpy of hydrate dissociation. In the current study we present a detailed overview of the calculation of the enthalpy of dissociation of carbon dioxide hydrates, focusing primarily on methods that are based on either the Clausius-Clapeyron equation or the direct calculation of the enthalpies of all the components that are involved in the hydrate dissociation reaction. Molecular Dynamics simulations are used extensively in order to calculate the enthalpies and molar volumes of water, carbon dioxide, and sI carbon dioxide hydrate (with variant degree of occupancy) at pressure and temperature conditions along the three-phase (either Hydrate – Liquid water – Vapour or Hydrate – Liquid water – Liquid CO₂) equilibrium line.



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P1.29 A Machine Learning Approach to Predict Gas Diffusivity in H₂O in a Wide Pressure & Temperature Range

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The diffusivity of light gases (e.g., CO₂, CH₄, O₂, H₂, etc.) in liquid H₂O over a wide range of temperatures and pressures is encountered in a plethora of industrial and environmentally-related processes and applications. Typically, when the measurement/estimation of a thermodynamic or transport property is required, three major routes are usually followed. Namely: (i) conducting experimental measurements, (ii) developing theoretical/semi-empirical models, and (iii) performing molecular simulations such as molecular dynamics (MD) or Monte Carlo (MC). In recent years an alternative approach has emerged, based on the utilization of Machine Learning (ML) methods.

The purpose of this study is twofold: (a) To conduct an extensive literature review for available values of diffusivities of light gases in liquid H₂O over a wide range of temperatures and pressures, and (b) To create a Machine Learning model based on the collected experimental/computational data achieving gas diffusivity in water prediction results of high accuracy.

To this extend, several classic Machine Learning methods such as Support Vector Machine (SVM), k-Nearest Neighbour (k-NN), Random Forest (RF), and ensemble ML as well, are compared in order to find the most suitable method for creating a robust prediction tool for describing the diffusivity of light gases in liquid H₂O. In addition, the obtained diffusivity dataset is enhanced with state-of-the-art techniques, to get predictions in sparse experimental areas (e.g., 0.1 MPa & temperatures higher than 350 K).



P1.30 Thermodynamic Study of Gas Mixtures to better understand the dynamics of the hydrates deposit in the Sea of Marmara

Experimental and Molecular Dynamics Simulation Approaches

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This study focuses on the thermodynamic behavior of gas mixtures sampled from the Sea of Marmara (SoM), which is crossed lengthwise by the northern branch of the North Anatolian Fault (NAF), a highly active seismic fault. The SoM is characterized by gas emission sites along the fault, as well as the discovery of gas hydrates in the Western High Basin. Given these particular geological features, the SoM represents a key region to investigate the relationship between gas emissions, seismic activity, and hydrate deposits. Analysis of complex thermogenic gases recovered from hydrate samples reveals a complex composition, including mainly methane (66.1%) with the highest concentrations of propane (18.8%) and isobutene (9.5%) ever recorded to date [1]. However, significant variations in composition have been observed among several samples taken from hydrate deposit sites and gas bubble streams, even within the same site, providing SoM as a unique setting for the study of hydrate stability.

To enhance our understanding of hydrate formation conditions and stability in the SoM, we investigate the influence of non-methane hydrocarbon on hydrate phase equilibria, through high-pressure lab experiments and Molecular Dynamics (MD) simulation. Hence, the first part of this study details new experiments conducted on binary and ternary gas mixtures aimed at updating the existing dataset. Here, the hydrate equilibrium point is defined as the point at which the last gas hydrate crystal dissociates, leaving the system in a vapor-liquid equilibrium. In addition, the Clausius-Clapeyron equation has been employed to



determine the hydrate equilibrium point for our gas mixture. The second part involves the MD simulations using GROMACS (version 2020.1) to predict the hydrate phase equilibrium of multi-component gas mixtures at different compositions and pressures, approaching the thermodynamic conditions of experimental samples. In our simulations, water and gas components have been described using the TIP4P/Ice model and united atoms force fields, respectively. The simulation outcomes of type sII hydrates are then compared with experimental data, forming a comprehensive analysis that bridges theoretical predictions with real-world observations.

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P1.31 Vapor-Liquid Equilibrium of electrolytic tertiary and quaternary mixtures

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The EleTher Joint Industry Project aims at understanding the salting-in vs salting-out behaviour of volatile compounds in mixed solvent systems. The applications related to this study are widespread as they range from distillation of products originating from biomass to stripping in metal recovery units. To that end, it has been proposed to investigate quaternary model system that contains water, an acid, a base and a cosolvent. The acid and base allow to cover a large pH range, while the solvent mixture allows tuning the dielectric constant and thus the ionic force of the solution.

The aim is to develop best practices for developing a thermodynamic model. To that end, it is essential to understand both chemical and phase equilibria that occur in the liquid phase. Electrolytic mixture can be complex due to interactions between ions and solvents.[1]

In this work, an aqueous solution of methanol, acetic acid and potassium hydroxide was investigated. Using ebulliometry, the boiling conditions of this system was investigated and compared with scattered literature data. The results show an unexpected shape of the bubble pressure as compared to the binary water-methanol system. Questions may also be raised regarding the stability of methanol in the presence of a strong hydroxide. The experimental results have been used for the parameterization of an electrolyte modelling approach considering simultaneously both phase equilibrium and chemical equilibrium.

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P1.32 Thermodynamics and formation mechanism of gas hydrates from multicomponent gas mixtures*O. Fandino¹, C. A. Agnissan^{1,2}, C. Guimpier^{1,2}, A. Desmedt², L. Ruffine^{1,3*}*¹ Geo-Ocean, Univ Brest, CNRS, Ifremer, UMR6538, F-29280 Plouzane, France² Institut des Sciences Moléculaires, UMR 5255 CNRS-Univ. de Bordeaux,
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Natural gas-hydrate systems are widely distributed on continental margins and represent one of the largest methane reservoir on Earth. They mitigate the release of huge amounts of methane into the water column from where it could migrate upwards, reach the atmosphere and contribute to the atmospheric methane budget; and they can trigger slope failure if they are brought the decomposition [1]. Natural gas hydrates also represent an energy source and sustain the development of unique chemiosynthetic ecosystems that colonize cold seep area. In most hydrate deposits, methane is overwhelmingly present as it originates from microbial processes. However, in some cases, the hydrates are formed from a multicomponent thermogenic gases and exhibit totally different properties, especially the thermodynamic ones that affect their stability and chemical composition.

In the present study, we have investigated both the thermodynamic stability and phase composition of complex gas hydrates as those of the hydrate deposit encountered in the Sea of Marmara. These hydrates are formed from a multicomponent gas mixture. Therefore, two gas mixtures were used, one collected on-site from gas bubbling at the seafloor in the Sea of Marmara and a commercial analogue. We employed GC analysis to monitor the composition change of the gas mixture over the course of the hydrate formation, Raman spectroscopy to reveal the structure and composition of the resulting hydrates, and modelling to assess their stability field. All these three technics show that propane and iso-butane are preferentially enclathrated within the hydrates, and this agrees with the results of previous study that directly characterized natural hydrate specimens collected within the sediment in the Sea of Marmara [2]. The modelling work explains why the hydrate deposit remains stable even with a seafloor temperature of 15 °C at the Sea of Marmara.



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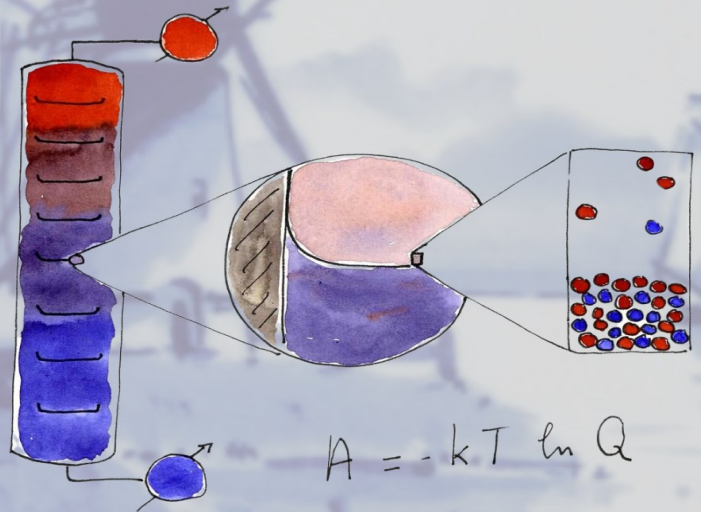
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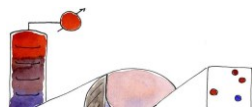


Poster Presentations

Day 2

P2.1 – P2.32





P2.1 Ultrasound Enhanced Diffusion In Hydrogels

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A major problem in cancer treatment based on chemotherapy, is the low and heterogeneous drug uptake in tumors. Encapsulating drugs into nanoparticles increases their accumulation in the tumor due to its hyperpermeable capillaries, and reduces toxic effects in normal tissue. However, the nanoparticles are heterogeneously distributed and mainly located close to the vessel walls in the tissue. After crossing the capillary wall, the nanoparticles have to penetrate through the extracellular matrix which consists of a collagen fiber network embedded in a hydrophilic gel of glycosaminoglycans, constituting a major barrier for successful delivery. Various strategies have been proposed to improve the delivery of drugs and nanoparticles for cancer treatment. One approach is the use of focused ultrasound, which has been shown to improve the delivery of drug-loaded nanoparticles [1]. In this work we have studied the focused ultrasound enhancement of nanoparticle diffusion using both experiments and non-equilibrium molecular dynamics [4].

Measurements from single particle tracking of 40 nm polystyrene nanoparticles in an agarose hydrogel with and without focused ultrasound was compared with a previous experimental study using 100 nm polystyrene nanoparticles [3]. In both cases we observed an increase in the mean square displacement during focused ultrasound treatment. We developed a coarse-grained non-equilibrium molecular dynamics model with implicit solvent to investigate the increase in the mean square displacement and its frequency and amplitude dependence. The model consisted of polymer fibers and two sizes of nanoparticles, and the effect of the focused ultrasound was modelled as an external oscillating force field. Comparison between the simulation and experimental results show similar mean square displacement trends, suggesting that the particle velocity is a



significant contributor to the observed ultrasound-enhanced mean square displacement. The resulting diffusion coefficients from the model was compared to the diffusion equation for a two-time continuous time random walk [2]. The model was found to have the same frequency dependency. At lower velocity amplitude values, the model has a quadratic relation with the velocity amplitude as described by the two-time continuous time random walk derived diffusion equation, but at higher amplitude, the model deviates, and its diffusion coefficient reaches the non-hindered diffusion coefficient. This observation suggests that at higher ultrasound intensities in hydrogels, the non-hindered diffusion coefficient can be used.

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P2.2 Competitive adsorption and transport of CO₂ and H₂O in CALF-20: a molecular simulation study

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Ecological concerns have led to increasing research efforts in the field of carbon dioxide capture and storage. In order to limit global warming in the next decades, capturing CO₂ from industrial emissions and/or air using nanoporous materials appears to be a promising solution. Metal Organic Frameworks (MOFs), in particular, show great potential due to their versatile structures and properties [1,2,3]. However, challenges remain, such as the ubiquitous humidity in flue gases known to usually induce deleterious effects in capture processes, by competing with CO₂ adsorption in sorbing materials [4,5]. Additionally, the diffusion mechanisms of CO₂ in the presence of water molecules are still poorly documented, yet crucial for improving capture beyond the only thermodynamic considerations [1]. Therefore, a deep study of the fundamental behaviours of these systems is essential in helping to select appropriate MOF candidates and the next sorbents design.

In this context, atomistic numerical simulations provide a better understanding of the thermodynamic and kinetic properties of CO₂ in these materials, helping in improving the capture process accounting for more realistic flue gases [2,5,6]. In this work, molecular simulations of CO₂ and water mixtures in CALF-20 (a recent structure by Shimizu *et. al.* showing promising properties for capture [7]), Fig. 1, are performed to explore the competitive adsorption between the species under a range of realistic temperature and pressure conditions. The mechanisms that control the diffusion of the molecules within the sub-nanometer pores of the MOFs are investigated through the determination of the Maxwell-Stefan diffusion coefficient, and the properties of the mixtures are compared to that of pure components.



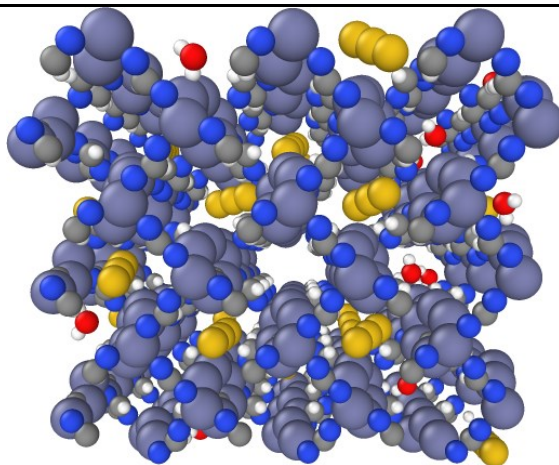
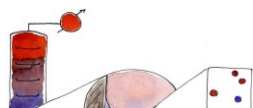


Fig. 1. Supercell (3x3x3) of CALF-20, in the presence of carbon dioxide (yellow) and water.

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P2.3 Predicting the solubility of amorphous and semi-crystalline polymers in organic solvents using SAFT- γ Mie EoS

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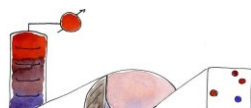
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Plastics are indispensable in modern commerce and industry, with their consumption projected to double in the next 20 years, according to the European Environmental Agency (EEA)¹. However, the environmental persistence of plastics and associated greenhouse gas (GHG) emissions are escalating concerns. Currently, most plastic recycling in Europe is mechanical, which is energy-intensive, inefficient at removing contaminants, and produces secondary-grade outputs. Solvent-based polymer dissolution is emerging as a promising solution, potentially reducing CO₂ emissions by 65-75% per ton of plastic waste compared to incineration².

This study investigates the robust thermodynamic modelling of polymer dissolution in organic solvents using polyethylene and polystyrene as case studies. We employ the SAFT- γ Mie³ equation of state to describe polymer-solvent mixtures. This thermodynamic model, with its group contribution approach, can accurately model various solvent systems with minimal parameters and experimental data. We consider organic solvents such as toluene, decalin, dodecane, cyclohexane, and xylene.

As an example, the different types of phase behaviour exhibited by mixtures of polyethylene and polystyrene are shown in Figure 1. The structural differences of the two polymers impose distinct thermodynamic treatments. Polyethylene is a semi-crystalline polymer, and as such requires a model considering solid-liquid equilibrium modelling for its solubility in solvents. In Figure 1a, the solvent effect on the 2000 g/mol polyethylene melting curve is plotted at the solvent vapour pressure, showing good agreement with experimental data. Toluene, n-dodecane, and decalin are considered as solvents.

In contrast, the solubility of amorphous polystyrene is analysed considering liquid-liquid equilibrium due to its lack of a crystalline structure. In Figure 1b, the cloud



curves, upper critical and lower critical solution temperatures (UCST and LCST, respectively) are plotted for the 37000 g/mol polystyrene and cyclohexane mixture at the solvent vapour pressure, which are also in good agreement with experimental data.

This work aims to demonstrate the robustness of SAFT- γ Mie when predicting polymer-solvent phase behaviour, providing a foundation for a computer-aided molecular and process design (CAMPD) study to optimize polymer dissolution.

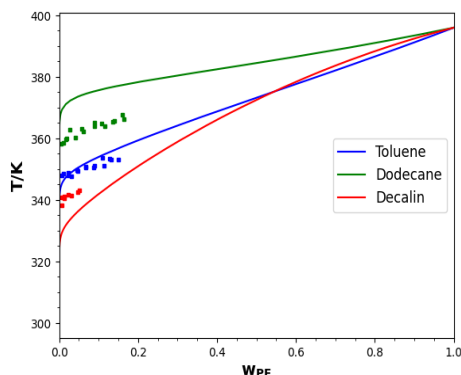


Fig. 1a. SAFT- γ Mie predicted solid-liquid equilibrium between 2000 g/mol polyethylene and solvents: toluene, dodecane, and decalin. $P = P_{vap}^{sol}$. Experimental data was measured as part of the current work through the Crystal16 Multiple Reactor.⁴

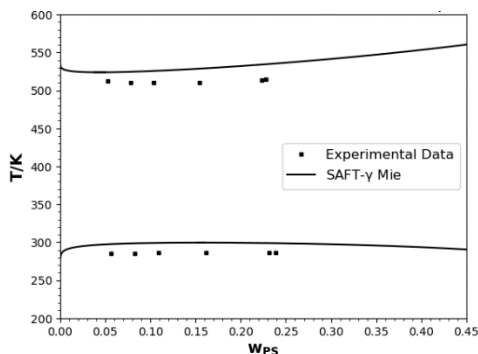


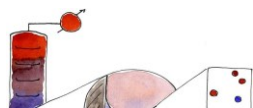
Fig. 1b. SAFT- γ Mie predicted liquid-liquid equilibrium between 37000 g/mol polystyrene and cyclohexane. $P = P_{vap}^{sol}$. Experimental data taken from Solms et al.⁵

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P2.4 Evaluation of a solid oxide fuel cell and vapor compression cooling system in a nearly zero energy building during summer period

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The building sector accounts for approximately 40% of the world's total energy consumption, with 50-70% of this consumption attributed to air conditioning systems [1,2]. In developed countries, building energy consumption is increasing more rapidly compared to developing countries [3]. As countries advance, the increasing demand for comfort conditions in buildings has significantly expanded the global market for indoor cooling applications [4]. In the ever-evolving competitive environment, solutions are being sought for questions like how to reduce energy consumption in buildings and alleviate the global energy shortage pressure [5]. These solutions are also being discussed under the increasingly popular concept of "nearly zero-energy buildings." Nearly zero-energy buildings, which imply the redevelopment of energy-efficient buildings, symbolize the trends in future buildings with low energy consumption and high indoor comfort features [6–9].

In recent years, to achieve zero-energy building goals, many researchers have focused on utilizing solar energy in cooling systems. A study presented by researchers at the National Renewable Energy Laboratory (NREL), a research unit of the United States Department of Energy, highlighted two major obstacles to the sustainable application of solar energy technologies in cooling technologies [10]. These are that 100% of the electricity required for cooling applications cannot be



supplied by solar energy technologies, and that very large installations are required to meet cooling needs with solar energy.

The limitations of using solar energy technologies highlight the need to develop more sustainable alternative energy technologies compared to solar energy applications in cooling systems. One such alternative technology is the integration of solid oxide fuel cells (SOFC) into cooling systems, which is considered a next-generation power generation technology due to its excellent energy conversion performance and low environmental emissions. Additionally, because SOFC units operate at high combustion temperatures, they help protect the environment [11,12]. SOFC units are flexible and can operate with many different types of fuels, one of which is biomass energy. Among all renewable energy sources, biomass energy is the fourth largest energy source in the world, meeting about 14% of the world's primary energy demand [13]. Therefore, the clean and efficient use of biomass energy has become an important topic in the field of renewable energy.

In this study, an SOFC unit using human waste, a type of biomass, as fuel was used to meet the 90 m² office building's electricity and cooling energy demands during working hours throughout the summer. The cooling process was carried out by a heat pump, and R600a was selected as the refrigerant. The schematic diagram of the system considered is presented in Fig. 1. For the analyses, the summer climate conditions of Izmir, Turkey, were considered (Fig. 2). Throughout the summer, the total electricity consumption by the compressor reached 255.72 kWh. The total electricity demand for the office and the cooling system was 1224.57 kWh. To meet this electricity demand, the SOFC needed to use 26.487 tons of syngas. The results obtained from this study are expected to inspire the widespread application of SOFCs for various academic and industrial purposes.

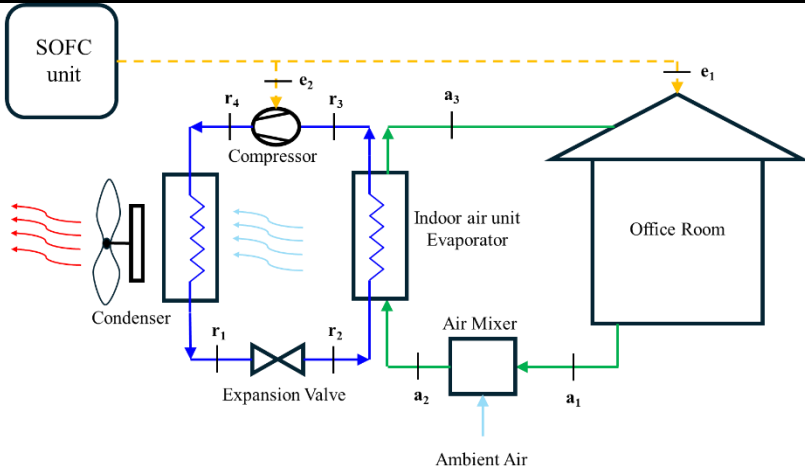
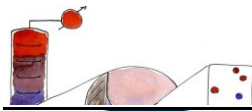


Fig. 1. Schematic view of SOFC assisted cooling system

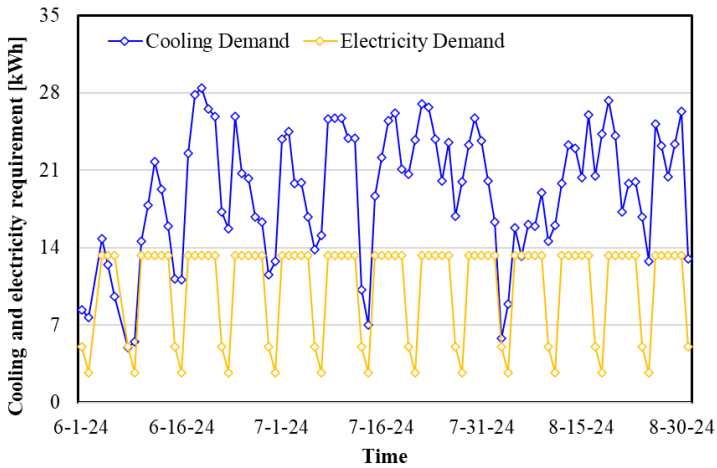


Fig. 2. Total daily cooling and electricity demand during summer period for an assumed 90 m² office room



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P2.5 Comparison of EOS-CG and GERG-2008 on a fluid flow model using CO₂ production data

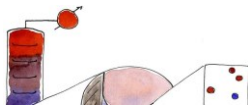
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CO₂ Capture and Storage (CCS) technology is currently the most promising method for transitioning between current anthropogenic CO₂ emissions and a zero-emissions scenario. Though the boundary conditions set by the capture and storage units have been the subject of much research, less interest has been paid to the challenges presented by the design and operation of full-scale transport networks [1]. The design and construction of a new CO₂ injection well is pivotal to guarantee the safety and the ability to contain the stored CO₂ for a long-term period. So, aiming to improve the understanding of the underlying multitude of physical phenomena occurring simultaneously during CO₂ injection, it is fundamental to validate and improve models that subsequently can be used to predict different configurations for which no experimental data exist, knowledge is uncertain, or further investigation is not feasible.

Considering the above, this work aims to evaluate two well-known thermodynamic models (GERG-2008 [2] and EOS-CG [3]) on a fluid flow model using CO₂ production data from the literature [4]. The flow model used is one-dimensional, consisting of single or multi phases, which can consist of N components, more information about the model can be seen in [5]. The data used was from Cranshaw and Bolling [4], with a composition of 97% of CO₂, but the other 3% is omitted in the paper, nevertheless, they point out that water is produced in the wellhead. Due to that, it was assumed three possible compositions (in mass fraction), which are: pure CO₂, CO₂ + water (0.3), and CO₂ + water (0.025) + methane (0.005). It was assumed a mass flow of 13.7 kg/s, well length of 914.3 m, and 0.0883 m of diameter. The flow model had a good representation of all three systems using both models. The average relative deviation (ARD) for the pressure along the well was ~2.3% (CO₂), ~3% (CO₂ + water), and ~1.5% (CO₂ + water + methane) for both models. For the temperature, the deviation was higher with an ARD of ~3.8% (CO₂), ~7.2% (CO₂ + water), and ~8.3% (CO₂ + water + methane) also for both models. In general, EOS-CG had a slitted smaller deviation than GERG-2008 for all cases, with a less than 1% difference between both models. It is important to highlight the lack of data for CO₂ well-flow and for CO₂ with



impurities. Only with accurate data, it will be possible to further develop and validate models used in well design.

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P2.6 Configuration of Nano-pore on Graphene Membrane and Hydrogen Separation: A Molecular Dynamics Study

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Graphene membranes with pores of less than 1 nanometre have attracted attention as hydrogen separation membranes and have been reported to exhibit high hydrogen selectivity and hydrogen separation properties¹. Since an efficient and purity hydrogen production method is a key to achieve hydrogen society, the nanoporous graphene membrane (NPG) is a leading candidate for hydrogen separation membrane. The bottom-up synthesis technique² allows us to design the optimal nano-pore configuration on graphene membrane for hydrogen separation. Therefore, this study clarifies the correlation between the configuration of nano-pores on graphene membrane and its separation property of hydrogen by using Molecular Dynamics (MD) method.

Figure 1 shows the constructed MD simulation system in which four different nano-pore configuration graphene membranes were applied (see Fig. 2). Mixing gas consist of 100 hydrogen molecules and 100 carbon dioxide molecules were considered in the constructed system. Pressure difference was created in the constructed system to produce the steady permeation flux by applying artificial force in the system (see Fig. 1). The pressure in the high-pressure side (left side of the membrane in Fig. 1) was 20 MPa. The temperature of system was controlled via Nosé thermostat at 300 K. The Lennard-Jones (LJ), coulomb, and harmonic potentials¹ were applied to the interaction of molecules. The three-body Tersoff and OPLS-AA potentials³ were applied to the NPGs. The cutoff distance and time step were set at 10 Å and 1.0 fs, respectively.

As results, we confirmed that the permeation flux of hydrogen molecules is much higher than that of carbon dioxide molecules. In addition, the permeability of hydrogen molecule clearly depends on the pore configuration and the permeability through the largest pore area is the highest.

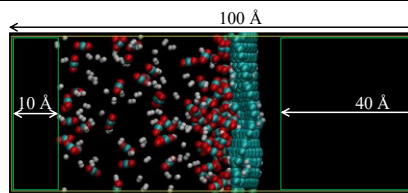
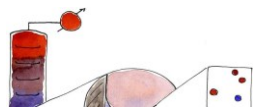


Fig. 1 Constructed MD simulation system. NPG was positioned at the center of the system. Artificial rightward force was applied on the molecules in the green frame region.

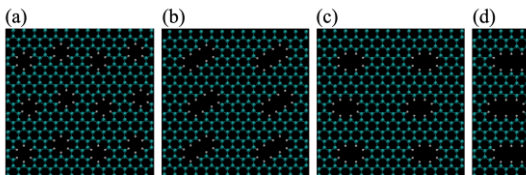


Fig. 2 Four types of NPG. (a) Simple basic pore. (b) Arranged two simple basic pores obliquely. (c) Arranged two simple basic pores at next lattice linearly. (d) Arranged two simple basic pores arranged at two lattices away linearly.

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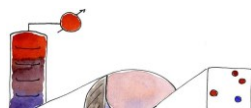
P2.7 Molecular Dynamics Insights into the Adsorption of Proteins on Carbon Nanotubes

*Qu Chen**

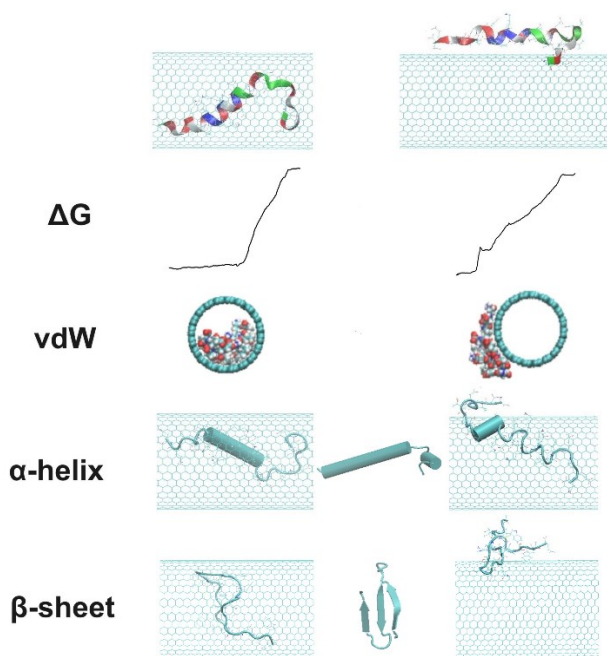
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Carbon Nanotubes (CNTs) can be considered as a potential platform for transmembrane drug delivery. Many experimental works have observed that CNTs can successfully help deliver bioactive molecules into living cells. However, for the rational design of an efficient CNT-based delivery system, it is essential to further understand the fundamental mechanism of the interaction between CNTs and protein/peptide drugs at molecular level. Our previous simulation studies have demonstrated that a drug molecule can either be spontaneously inserted into CNTs with decreased free energy of the system¹, or be attached onto the surface of CNTs inducing stepwise conformational change². This work aims to make a comprehensive comparison of these two adsorption processes. To this end, we performed molecular dynamics simulations to explore the interaction energy, conformational changes, and free energy changes of proteins containing α -helices or β -sheets interacting with the inner and outer surfaces of CNTs. Our simulation results indicate that a protein experiences slightly stronger van der Waals interactions with the inner walls of CNTs than with the outer walls. However, the surface curvature plays a significant role in influencing the protein's conformations. Specifically, most of the protein's α -helix structure is likely to be affected on the CNT exterior but to be retained on the interior³, while the protein's β -sheet content tends to be lost, partially or entirely, on both the interior and the exterior. Thirdly, the Molecular Mechanics – Poisson Boltzmann Surface Area (MM-PBSA) analysis reveals the key role of the protein's aromatic residues, which may guide the change of the protein's secondary and tertiary structures upon its adsorption on the tube surface. Finally, the umbrella sampling-based and Jarzynski equality-based free energy profiles consistently show that, for a CNT with an appropriate size, it is thermodynamically more favourable for the protein to be loaded onto the inner tube wall than the outer tube wall, primarily due to a larger free energy change for the former strategy, but unloading the drug from the tube interior poses greater challenges. This work not only provides a comprehensive



guideline for the design of a protein-CNT complex, but also raises great concerns over the toxicity and biocompatibility of curved nanomaterials.



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P2.8 Experimental and thermodynamic modelling study of gas hydrate formation and inhibition in CCUS applications

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Sequestration of CO₂ in subsurface geological formations offers significant potential to reduce atmospheric carbon contents. In this regard, low-pressure depleted natural gas reservoirs are a promising target. However, injection of dense CO₂ into these reservoirs poses some unresolved injectivity challenges due to low temperatures caused by isenthalpic expansion of the injected fluid and phase changes from liquid to gaseous CO₂. Associated with low temperatures, hydrate formation is considered as one of the major risks for implementation of CO₂ injection in depleted gas reservoirs. In this study, scenarios of near-wellbore hydrate formation are investigated in a series of laboratory experiments, with the aim to mitigate the impact of CO₂ hydrates on injectivity.

In our experiments, we investigate hydrate formation and dissociation in sandstone cores with experimental conditions varying from 0°C to 30°C and from 0 to 40 bars. Key factors examined included water saturation levels, brine salt types and concentration, and the inherent permeability of sandstone. The result reveals that permeability and pore size play important roles in hydrate formation. The obvious decrease in injectivity occurs in low permeable rock (Bandara) around 40% water saturation, which was induced by the hydrate formation. The low permeable core shows stronger hydrate reactions than higher permeable cores. CT images indicate that hydrate formation and dissociation enhance the uniformity of water distribution in the core. These experiments were complemented by micromodel investigation with precise control over thermodynamic conditions for hydrate formation and dissociation. High-resolution cameras enabled the dynamic capture of pore-scale hydrate formation and dissociation, with kinetics quantified accordingly.

Experiments were designed with the aid of DARTS-flash, our in-house thermodynamic library that is primarily developed to perform flash and



thermodynamic property calculations for simulation of flow and transport in subsurface energy transition applications. This study serves to validate the thermodynamic modelling approach and present the DARTS-flash package for computing multiphase equilibria involving a wide range of reservoir fluids, solids and chemicals, particularly in relation to formation, dissociation and inhibition of gas hydrates.



P2.9 Calculation of thermodynamic properties of helium and neon by path integral Monte Carlo simulations using *ab initio* potentials

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The accurate theoretical prediction of thermodynamic properties of atoms and molecules with small mass such as helium and neon requires the consideration of quantum effects of the nuclei. Path integral simulations, based on Feynman's formulation of quantum mechanics, provide a method to treat nuclei quantum-mechanically within a classical simulation without uncontrolled approximations. We apply the method of Lustig [1] to derive expressions to calculate arbitrary thermodynamic properties such as the speed of sound or Joule-Thomson coefficient within these path integral simulations. They are performed for neon and helium using highly accurate *ab initio* potentials accounting for both pairwise and non-additive three-body interactions [2-5]. We validate our method for both fluids on the supercritical 80 K isotherms and observe an excellent agreement with recent, precise experimental speed-of-sound data [6] confirming our approach. With the developed framework it is possible to predict thermodynamic properties in regions with only limited or less accurate experimental data such as in the liquid phase of neon. We additionally perform semi-classical simulations applying the Feynman-Hibbs correction for quantum effects. The comparison of these results with those of path integral simulations allow us to assess the validity of this correction within the studied temperature and pressure ranges for both investigated fluids. Additional classical simulations enable the evaluation of the contribution of non-additive three-body interactions and quantum effects to different thermodynamic properties.

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P2.10 Thermodynamic Analysis of Cryogenic Hydrogen Storage Systems for Heavy-Duty Trucks

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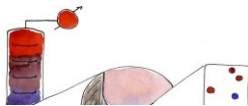
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As the world transitions towards more sustainable energy solutions, hydrogen-powered heavy-duty trucks emerge as a key component in reducing CO₂ emissions and promoting clean energy in the transportation sector. Therefore, storing hydrogen efficiently onboard these vehicles is crucial for the competitiveness of hydrogen-powered transportation. One solution to achieve higher storage densities and, thus, longer driving ranges is to store hydrogen at cryogenic temperatures as subcooled liquid hydrogen (sLH₂) or at cryogenic temperatures and high pressures as cryo-compressed hydrogen (CcH₂).

In this study, we investigate the thermodynamic behavior within cryogenic hydrogen tanks, focusing on typical operating scenarios in heavy-duty truck applications, such as discharge, dormancy, and refueling. We employ a differential-algebraic equation system, based on earlier studies [1,2], that includes energy and mass balances, the caloric equation of state, and several algebraic equations. This equation system can describe the thermodynamic state of the hydrogen within the tank at any time and in any operational mode. It allows for the simulation of processes within the single- and two-phase regions using the same equation system. Only three equations are automatically switched by a smart decision logic when the operational mode changes or the two-phase region is entered or left.

To enable simulations within the two-phase region, we use the property c_{v2P} from the property data program REFPROP [3], which can be understood as a specific isochoric heat capacity within the two-phase region. To further understand the thermodynamic significance of this property, we derive its definition starting from the energy balance of the hydrogen in the two-phase region.

Finally, we demonstrate the model by applying it to cryogenic hydrogen tanks of heavy-duty trucks. By simulating typical driving cycles and analyzing the heat transfer and phase change processes within these storage systems, we gain significant insights into the thermodynamics in such hydrogen storage tanks. This



allows us to draw preliminary conclusions regarding optimal operation strategies for heavy-duty hydrogen trucks.

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P2.11 Integrating Machine Learning and Molecular Simulations to Improve H₂S Uptake on MOFs

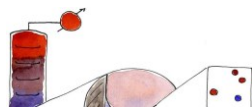
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Approximately, nearly half of the global natural gas (NG) reserves contain hydrogen sulfide (H₂S) at levels as high as 20%, rendering it sour. Before proceeding with any downstream processes, it is essential to sweeten the NG to eliminate H₂S due to its toxicity, corrosiveness, and negative impact on combustion efficiency. A promising technology for this purpose is the utilization of Metal-Organic Frameworks (MOFs). This study focuses on developing and optimizing machine learning (ML) models to screen MOFs for H₂S loading capacities. In this exploration process, the ab initio REPEAT charge MOF (ARC-MOF) database, encompassing approximately 280,000 experimental and hypothetical MOFs, is investigated using ML models trained with geometric and atomic features, as well as SMILES descriptors. We evaluate the performance of the Atomic-Property-Weighted Radial Distribution Function (AP-RDF), Revised Autocorrelation Function (RAC), and Materials Agnostic Platform for Informatics and Exploration (MAGPIE). We developed an iterative ML process that yielded an R² of 0.95 using a combination of geometric and atomic features, using the Light Gradient Boosting (LGBM) ML module. Upon deploying this model on the entire database, the predicted top 300 performing structures were validated against computed uptake capacity using Grand Canonical Monte Carlo (GCMC), resulting in an R² of 0.84. Furthermore, the same model was validated on an isolated test set comprising 309 representative structures, yielding an R² of 0.91. Overall, we developed an accurate ML model that predicts H₂S uptake capacity with 91% accuracy at a negligible computational cost compared to molecular simulation. Our methodology can be applied to study other gases on nanoporous materials.



P2.12 Predicting the water adsorption isotherm step in Covalent Organic Frameworks

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Atmospheric water harvest using porous materials is an attractive solution to water crisis and in indoor dehumidification. Over the past years, there has been a growing focus on exploring the potential of Covalent Organic Frameworks to fulfil this objective. Here, we propose a simulation protocol that can help predict the inflection point/step of the water adsorption isotherm, one of the critical indices to look for.

Grand Canonical Monte Carlo (GCMC), the conventional simulation setup for studying gas adsorption in porous systems, proves to be computationally very expensive in the case of water. Hence, we implement a flat histogram method, NVT+w [1-2], with interpolation, to obtain the water isotherms. Using this method and the corrected saturation pressure of water, the step positions obtained from the simulations matched well with the experiments for several COFs [3-6] possessing a diverse set of linker groups. Therefore, this methodology can be used in screening COFs for their water-harvesting properties.

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P2.13 Molecular Understanding of the Solute-Hydrotrope Aggregation in Aqueous Solutions: A Molecular Dynamics Approach

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Hydrotropy is a phenomenon where an amphiphilic molecule (i.e., the hydrotrope) is able to enhance the aqueous solubility of a hydrophobic solute. Understanding the molecular mechanisms underlying this process is essential to design novel hydrotropes to optimize solubilization processes of poorly soluble compounds. As such, this study investigates the hydrotropic behavior of 1,2-alkanediols in enhancing the aqueous solubility of syringic acid using molecular dynamics (MD) simulations. The analysis carried out here employs, in particular, Kirkwood-Buff integrals (KBI), solvation free energies, and radial distribution functions (RDF). Both the hydrotropes and solute were chosen based on their sustainable character and previous use in hydrotropic processes.

The GAFF2 force field and SPC/E water model were used to study the system. The charge distributions for the 1,2-alkanediols and syringic acid were obtained using the RESP2(0.5) methodology [1] to account for the polarization of the molecules in the solvents. This combination of force fields successfully reproduced the experimental KBI values in binary mixtures of 1,2-ethanediol + water and 1,2-propanediol + water.

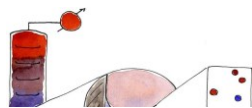
Solvation free energy calculations underscore the thermodynamic favorability of syringic acid solubilization in the presence of 1,2-alkanediols, aligning with experimental trends [2]. The MD simulations reveal a pronounced affinity between syringic acid and the 1,2-alkanediols, particularly at low hydrotrope concentrations. KBI analysis indicates preferential solvation of syringic acid by the hydrotropes, suggesting a significant shift in local solute-solvent structure. The RDF data shows higher peak intensities and specific interaction



patterns between the aliphatic chains of the alkanediol molecules and syringic acid, corroborating that the apolar moieties of the hydrotrope aggregate around the hydrophobic solute molecule [3].

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P2.14 Prediction of Adsorption Properties using Classical Density Functional Theory

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Reducing environmental impacts and cost of separation processes calls for more energy-efficient technologies. Currently, separations preferentially employ distillation, but alternative processes are being investigated such adsorption. In particular, adsorption based on Metal-organic frameworks (MOFs) offers a great potential to improve separations due to their large surface area and the infinite materials design space, offering the possibility to tailor MOFs for particular applications. Experimentally exploring this material design space is prohibitive. Computations screening approaches have therefore been developed for predicting material properties and ranking the materials by key performance indicators [1]. However, established methods for material property prediction, like Grand Canonical Monte Carlo (GCMC) simulations, can still take hours to days to predict full adsorption isotherms, an important property for MOF-based separation processes. This computational expense constrains screening processes to a limited number of materials. Thus, developing methods to predict adsorption properties with reduced computational efforts could substantially enhance the throughput of material screening.

In this work, we apply three-dimensional classical density functional theory (3D-cDFT) [2] for fast and accurate prediction of adsorption properties of methane, nitrogen, and carbon dioxide. We demonstrate the ability of 3D-cDFT to reproduce adsorption isotherms and enthalpies of adsorption calculated by GCMC simulations while reducing CPU time by two orders of magnitude, leading to adsorption properties being computed on average in six minutes. The 3D-cDFT method used here, using the FeOs software [3], employs a structural configuration of the solid material, a force field characterization of the solid-gas interactions, and



a Helmholtz energy functional derived from the PC-SAFT equation of state [4] to model the gas phase. Particularly, this approach does not necessitate additional fitting for novel structures, thereby achieving the level of generalizability required for large-scale screenings.

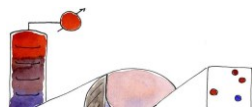
Our results indicate that 3D-cDFT is a viable method for high-throughput screening of adsorbent materials and could therefore enhance the exploration of the materials design space.

Acknowledgements

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P2.15 Calculating Thermodynamic Factors for Diffusion Using the Continuous Fractional Component Monte Carlo Method

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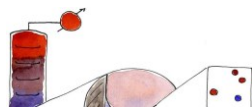
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Thermodynamic factors for diffusion connect the Fick and Maxwell–Stefan diffusion coefficients used to quantify mass transfer. Activity coefficient models or equations of state can be fitted to experimental or simulation data, from which thermodynamic factors can be obtained by differentiation. The accuracy of thermodynamic factors determined using indirect routes is dictated by the specific choice of an activity coefficient model or an equation of state. The Permuted Widom’s Test Particle Insertion (PWTPI) method developed by Balaji et al. enables direct determination of thermodynamic factors in binary and multicomponent systems. For highly dense systems, for example, typical liquids, it is well known that molecular test insertion methods fail. In this article, we use the Continuous Fractional Component Monte Carlo (CFCMC) method to directly calculate thermodynamic factors by adopting the PWTPI method. The CFCMC method uses fractional molecules whose interactions with their surrounding molecules are modulated by a coupling parameter. Even in highly dense systems, the CFCMC method efficiently handles molecule insertions and removals, overcoming the limitations of the PWTPI method. We show excellent agreement between the results of the PWTPI and CFCMC methods for the calculation of thermodynamic factors in binary systems of Lennard-Jones molecules and ternary systems of Weeks–Chandler–Andersen molecules. The CFCMC method applied to calculate the thermodynamic factors of realistic molecular systems consisting of binary mixtures of carbon dioxide and hydrogen agrees well with the NIST REFPROP database. Our study highlights the effectiveness of the CFCMC method



in determining thermodynamic factors for diffusion, even in densely packed systems, using relatively small numbers of molecules.



P2.16 Glycine solvation study

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Understanding solvation dynamics is crucial in various scientific fields, ranging from biochemistry to materials science. Solvation involves the interaction of solute molecules with a solvent, which significantly influences the properties and behavior of the solute. This is particularly relevant in aqueous solutions.

Glycine is the simplest amino acid, that can exist in zwitterionic and neutral form. Studying glycine's solvation dynamics, especially in its zwitterionic form, provides insights into the behavior of more complex amino acids and peptides in aqueous environments. We studied behavior of glycine in the range of temperatures, starting from supercooled water at 238 K and up to 298 K. The effect of the concentration of zwitterion molecules was also taken into account, in the range from 5 to 30%.

Solvation is inherently complex, traditional experimental methods often provide limited insights into the molecular details of solvation shells. Kirkwood-Buff Integrals help to overcome these limitations. The data for KBIs was taken from molecular dynamics simulations, performed using NPT ensemble. The values of KBIs were obtained using 2 methods: integration over the radial distribution function (RDF) and calculation of fluctuations in the particle number [1]. Using values of KBIs for 2 component systems we derived such characteristics as partial molar volume of water and glycine, isothermal compressibility, and thermodynamic correction factor(Γ)(Figure 1.) [2]. The energy fluctuations were calculated using the small system method.

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P2.17 Incorporating material flexibility effects into adsorption modelling using non-local Density Functional Theory

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The study of adsorption in nanoporous materials using classical density functional theory (DFT) has proved particularly fruitful, both as a framework for characterizing adsorbents using gas porosimetry [1] and as a tool for predicting adsorption under conditions of higher temperatures and pressures [2]. However, DFT framework is naturally derived in the Grand Canonical ensemble, which is only suitable for fluid adsorption in rigid frameworks. Hence, only a very limited number of DFT-based studies addressed the flexibility of the porous network [3,4]. Here, we aim at modeling adsorption in flexible or switchable nanoporous materials with a cDFT framework through an osmotic potential, inspired by the strategy developed by Coudert and coworkers [5,6] with Monte Carlo molecular simulations.

As a first step, the adsorption in a material presenting two distinct shapes (large-pore and narrow-pore) is investigated as a representative example of breathing metal-organic frameworks (such as MIL-53). The adsorbed fluid is described with a Non-Local-DFT/SAFT coupling [7,8]. The simplified MIL-like material consists in evenly distributed and identical Lennard-Jones atoms in a 3D space, as what was done in [6] (see Fig a). By using a bi-stable (Fig b) with varying intensity, we show that we can obtain different adsorption-swelling behaviours, including the known MIL breathing (Fig c). The second step consists in considering the real atomistic MIL-53 structure and compare the NLDFT results with experimental adsorption data.

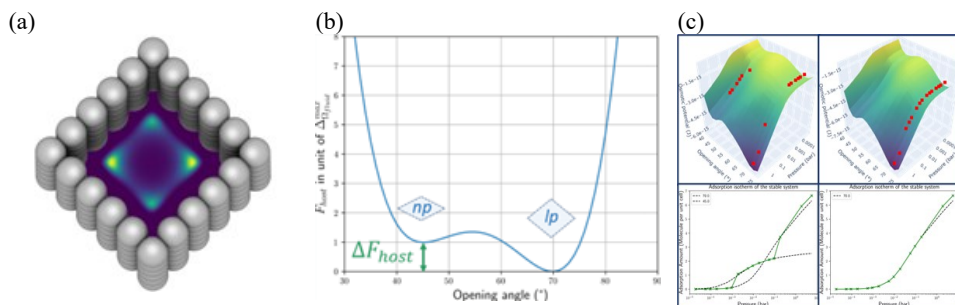
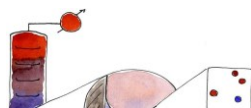


Fig 1c. (top) 3D views of the osmotic Grand Potential ; squares represent the minimum at a given pressure ; (left) breathing behavior (right) ΔF_{host} too strong to breathe. (bottom) Adsorption isotherms considering minimum Ω_{os} for each pressure.

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P2.18 Multiscale Modelling of Transport Properties of KOH (aq) with Machine Learning

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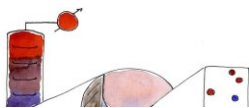
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Aqueous potassium hydroxide (KOH(aq)) exhibits an exceptionally high electrical conductivity, which is crucial for various industries reliant on efficient electrolytes. This increased conductivity arises from the Grotthuss mechanism, where hydroxide ions exchange protons with water molecules. Applications of KOH(aq) range from alkaline water electrolysis to electrochemical CO₂ reduction. State of the art classical force fields for molecular dynamics fails to predict OH⁻ diffusion correctly, as these cannot capture the Grotthuss mechanism.^[1] Ab initio molecular dynamics (AIMD) captures the proton transfer, but is limited by short timescales and small system sizes. Machine learning force fields (MLFF) have emerged as a promising solution, offering access to much longer simulation times and near-AIMD accuracy. In this work, an MLFF capable of accurately capturing OH⁻ transport behaviour is constructed. Structural properties of AIMD and MLMD simulations are compared to ensure accuracy of the MLFF. Graph theory is applied to generate 2D representations of the molecular structures,^[2] which are used to analyse the hydration of OH⁻ during proton hopping events. This method distinguishes two hydration modes, i.e., the reactive and inactive modes, which supports the qualitative findings of Tuckerman et al.^[3] MLMD simulations at experimental density, 345 K, and 1 mol KOH per kg of water, yield a self-diffusion coefficient for OH⁻ ions of $(6 \pm 2) \times 10^{-9}$ m²/s, closely matching the experimentally-found value 5.27×10^{-9} m²/s. The computed electric conductivity of (29 ± 6) S/m overlaps with the experimentally determined conductivity of 26 S/m as well. Our work not only advances the understanding of OH⁻ transport, but it also shows the



effectiveness of ML in molecular simulations. It demonstrates the potential of MLFFs to bridge the gap between classical MD and AIMD simulations, and highlights the utility of graph theory in understanding molecular structures, while offering valuable insights for industries reliant on efficient electrolyte.

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P2.19 Molecular Simulation of the Phase Behaviour of Attractive Polymers

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Through a hierarchical modeling scheme, we determine a phase diagram of attractive, fully flexible and rod-like polymer chains in two and three dimensions [1,2]. All systems are generated, equilibrated and successively analyzed through the Simu-D software [3]. A surprisingly rich collection of distinct crystal polymorphs appears, which can be finely tuned through the range of attraction and chain stiffness. In three dimensions these include the face centered cubic, hexagonal close packed, simple hexagonal and body centered cubic crystals and the Frank-Kasper phase [4]. A simple geometric model is proposed, based on the concept of cumulative neighbours of ideal crystals, which can accurately predict most of the observed structures and the corresponding transitions. A geometrical analysis is provided on the characteristics of the self-assembled polymer clusters and crystals under conditions that correspond to vacuum. The present work demonstrates, at a fundamental level and by utilizing highly idealized model, how proper fine tuning of selected parameters can be used for the design of polymer crystals with tailored morphologies and structural characteristics.

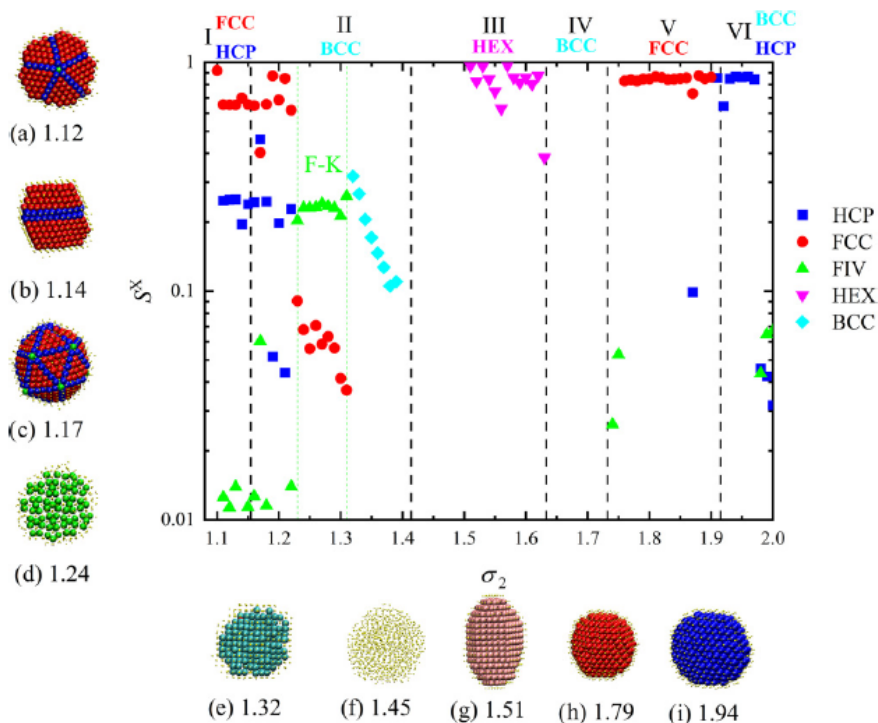
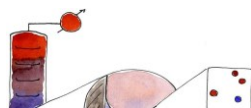


Fig. 1. The phase behavior of fully flexible attractive chains as a function of the attraction range in three dimensions. Also shown on the left and bottom are typical configurations established at the end of the MC simulations. Predictions of the geometric neighbor model are reported on the top of the graph where roman numbers identify regions where a specific crystal is expected to prevail. The vertical dashed lines identify the thresholds between different regimes

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P2.20 Monte Carlo simulations of H₂ adsorption on MOF-5 halogenated derivatives

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In recent years, the growing concern about the environmental impact and limited availability of fossil fuels has led to hydrogen emerging as a promising candidate due to its environmental benefits, potential for renewable production, and high gravimetric energy density (i.e., three times higher than traditional fossil fuels). Unfortunately, some technical and economic challenges remain, one of which is related to its safe storage. Among all available alternatives, metal-organic frameworks (MOFs) have been explored as potential adsorbents for hydrogen storage, with efforts focused on modifying their structure to achieve high uptakes of the adsorbate. However, a structural modification of MOFs that allows the Department of Energy (DOE) goals to be achieved, especially at ambient temperatures, has yet to be found.

In this contribution, we have performed simulations with RASPA [1] to evaluate the H₂ adsorption capabilities of halogenated derivatives of IRMOF-1 (MOF-5), which have shown excellent performance for noble gases [2]. Specifically, we carried out GCMC simulations to calculate the adsorption isotherms, heats of adsorption, Henry constants and textural properties in pristine IRMOF-1. Then, we compared its performance with its derivatives (IRMOF-2-X), replacing a single H atom in each linker with a halogen (X = F, Cl, Br, or I). In all simulations, the MOFs and hydrogen molecules were treated as rigid bodies, and their interaction was modeled using a Lennard-Jones potential. Feynman-Hibbs corrections based on the Darkrim-Levesque model were also applied to H₂ [3]. Preliminary results suggest that IRMOF-2-Br has a higher volumetric capacity than pristine IRMOF-1 at pressures up to 4 bar, but at higher pressures, the trend reverses, leading to decreased adsorption. This observation aligns with the reduction of pore size in IRMOF-2-Br and the values of adsorption enthalpies at infinite dilution for these systems, resulting in a slight increase in the halogenated structure (2.53 kJ mol⁻¹ for IRMOF-1 and 3.08 kJ mol⁻¹ for IRMOF-2-Br). The gravimetric capacity of IRMOF-2-Br consistently shows lower adsorption than



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pristine IRMOF-1 across the entire pressure range, as depicted in Fig(1a). These findings emphasize the need to consider functionalization effects on the performance and properties of hydrogen storage materials.

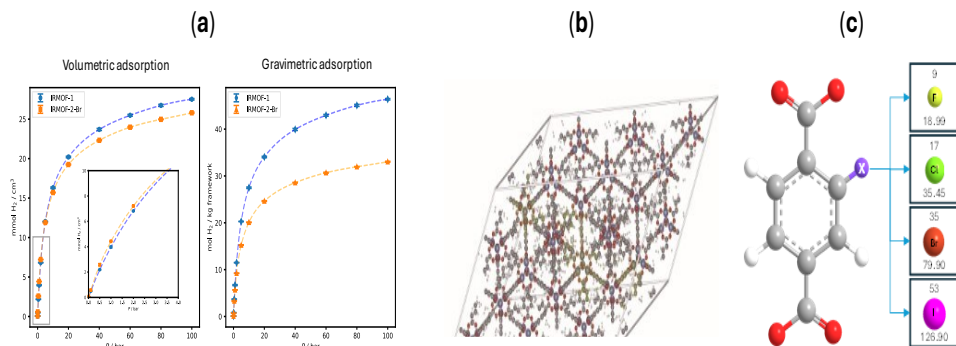
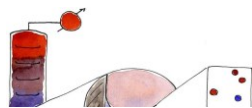


Fig. 1. (a) Simulated adsorption isotherms at 77.15 K for IRMOF-1 and IRMOF-2-Br. (b) iRASP [4] Snapshot of IRMOF-1 structure and adsorbed H₂ molecules at 77.15 K and 10 bar (c) Organic linker (terephthalate) and the proposed modifications of the linker

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P2.21 Solubility measurements and thermodynamic modeling of dipeptides in binary solvent mixtures

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Following the monumental achievement of discovering insulin to treat diabetes in 1921, development of therapeutic peptide drugs accelerated and they currently account for a significant proportion of the pharmaceutical market with worldwide sales of \$48 billion in 2022. Accurate prediction of peptide's solubility is crucial for decision making at different stages of peptide-drug development such as drug discovery, drug design, peptide synthesis and sequence-structure modification. Experimental measurements of the peptide's solubility are challenging as they are poorly soluble in organic solvents and phase transitions leading to non-equilibrium formation of gels is observed. From a modelling standpoint, molecular approaches can deliver accurate predictions of complex phase behaviour, including solid–liquid solubility and liquid–liquid de-mixing, and can account for detailed molecular features. These approaches can provide reliable solubility predictions when accurate experimental data of melting properties of peptides and activity coefficients of the peptides in solvents are available. We implement SAFT- γ Mie [1] which is a group-contribution approach based on a heteronuclear model of fused segments interacting via Mie potential. These segments also feature association sites when necessary to model directional interactions that mimic hydrogen bonds. The approach has been shown to deliver accurate predictions of the solubility of pharmaceuticals including the pH-solubility profiles of ionisable active ingredients. [2], [3]. Since peptides usually have a high melting temperature and thus decompose during slow heating in the experiments, it makes the direct measurements of these properties a challenge. Measuring the solubilities of one peptide in a range of solvents can lead to development of better models that can



help in the determination of melting properties possible by fitting once we have theoretical models with high accuracy predictive capabilities. We use Crystal16, a multi-reactor crystalliser, to measure the solubility of diglycine, dialanine, alanylglycine and glycyl-L-alanine in pure water and binary solvent mixture consisting of water and primary and secondary alcohols in a range of temperature (260 - 360 K) and at different weight ratios of the two solvents. The results indicate that the solubility of diglycine decreases as alcohol concentration increases in the solution. The solubility of diglycine decreases with increasing the chain length of the alcohol. The presence of alanine amino acid in the dipeptide structure leads to higher solubility in all the solvent mixtures considered. SAFT- γ Mie theory is used to predict the solubility of these dipeptides in water to assess the predictive ability of current model with the experimental data obtained. We extend the development of current models to predict the solubility of dipeptides in the binary solvent system of water + alcohol. These predictions in turn help in assessing the reliability of experimental data available for melting properties of peptides.

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P2.22 Thermophysical Properties and Phase Behavior of CO₂ with Impurities: Insight from Molecular Simulations

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Carbon Capture and Storage (CCS) is widely used in industries to meet CO₂ emission targets. Carbon capture and sequestration depends on safe and economical transportation of CO₂. The captured CO₂ will contain various impurities in different concentrations based on the source and capture technology. Impurities significantly alter the thermophysical properties of CO₂, affecting the flow behavior, pipeline capacity, and operating conditions in CO₂ transportation systems.[1] Experimentally determining thermophysical properties for various compositions commonly found in CO₂ transportation systems is extremely challenging. To overcome this challenge, we performed Monte Carlo (MC) and Molecular Dynamics (MD) simulations of CO₂ rich mixtures to compute thermophysical properties such as densities, thermal expansion coefficients, isothermal compressibilities, heat capacities, Joule-Thomson coefficients, speed of sound, and viscosities at temperatures (235-313) K and pressures (20-200) bar. We computed thermophysical properties of pure CO₂ and CO₂ rich mixtures with N₂, Ar, H₂, and CH₄ as impurities (1-10) mole%. Our results show that computed thermophysical properties of pure CO₂ and CO₂ rich mixtures are in good agreement with Span and Wagner Equation of State (EoS)[2] and GERG-2008 EoS[3], respectively. Our findings show that mixtures with a molecular weight lower than pure CO₂ have lower densities than pure CO₂. We showed that impurities decrease the values of thermal expansion coefficients, isothermal compressibilities, heat capacities, and Joule-Thomson coefficients in the gas phase, while these values increase in the liquid and supercritical phases. In contrast, impurities increase the values of speed of sound in the gas phase and decrease in the liquid and supercritical phases. We present an extensive data set of thermophysical properties for CO₂ rich mixtures with various impurities, which will help to design the safe and efficient operation of CO₂ transportation systems.



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P2.23 Understanding Shape Selectivity Effects of Zeolites on Hydroisomerization of Alkanes at Reaction Equilibrium

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In this work, the role of zeolite shape selectivity in the hydroisomerization of linear alkanes is studied. Hydroisomerization reactions transform linear hydrocarbons to branched hydrocarbons which are important in applications such as production of sustainable aviation fuels via CO₂ reduction or bio-components. It is important to comprehend the role of chemical equilibrium of these reversible reactions to investigate conditions that can potentially optimize the production of branched hydrocarbons and minimize the cracking reaction products.¹ We analyze the shape selectivity effects of FAU-, ITQ-29, BEA-, MEL-, MFI-, MTW-, and MRE-type zeolites on the hydroisomerization of C₇, and C₈ isomers at reaction equilibrium³. The reaction equilibrium distribution of hydroisomerization reactions is obtained by enforcing chemical equilibrium in the gas phase and phase equilibrium between the gas and the adsorbed phase components.^{1,2} This approach mimics the reaction equilibrium distribution in the adsorbed phase (Fig. 1). Using the Henry's law at infinite dilution and mixture adsorption isotherm models at elevated pressures, the adsorbed loadings are calculated from the chemical equilibrium conditions in the gas phase. Multi-branched isomers are favored in cage-like pore structures (Fig. 2c) such as ITQ-29-type zeolite (Fig. 2a), while mono-branched isomers are preferred in channel-like pore structures (Fig. 2d) such as MEL-type zeolite (Fig. 2b)³. The gas phase pressure has a negligible effect on the reaction equilibrium of C₇ isomers, especially at high temperatures (500 K or above)³. For hydroisomerization of alkanes longer than C₁₀ (Fig.3), the thermochemical properties of alkanes required to compute the gas phase equilibrium distribution are predicted using a



linear regression model which uses tables by Scott⁴ as the training dataset. It uses second order group contributions to account for the interactions between the neighboring groups of atoms. In the future studies, the predicted thermochemical properties will be used to compute the reaction equilibrium distribution of hydroisomerization of long chain alkanes such as C₂₀.

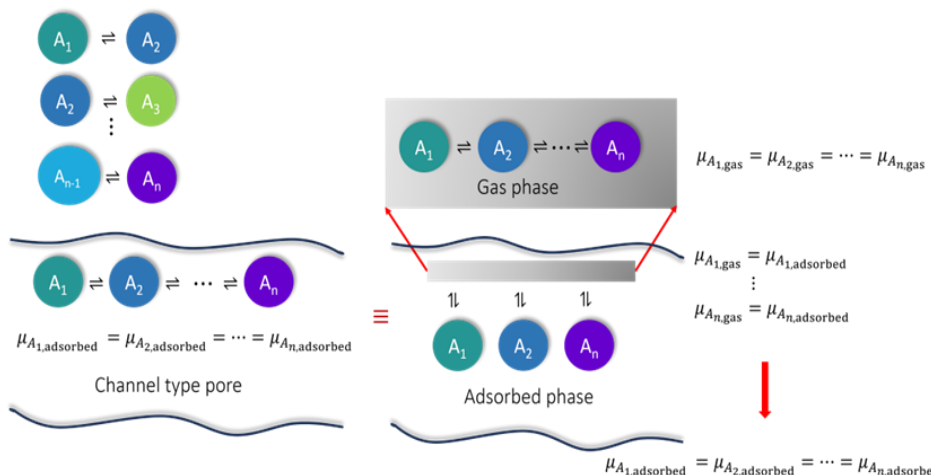


Fig. 1. Schematic representation of the modeling framework for computing the reaction equilibrium distribution in the adsorbed phase. Chemical equilibrium is enforced in the gas phase for a system comprising of isomers A_1, A_2, \dots , etc. Phase equilibrium between the gas and the adsorbed phase will ensure the establishment of chemical equilibrium for the components in the adsorbed phase.

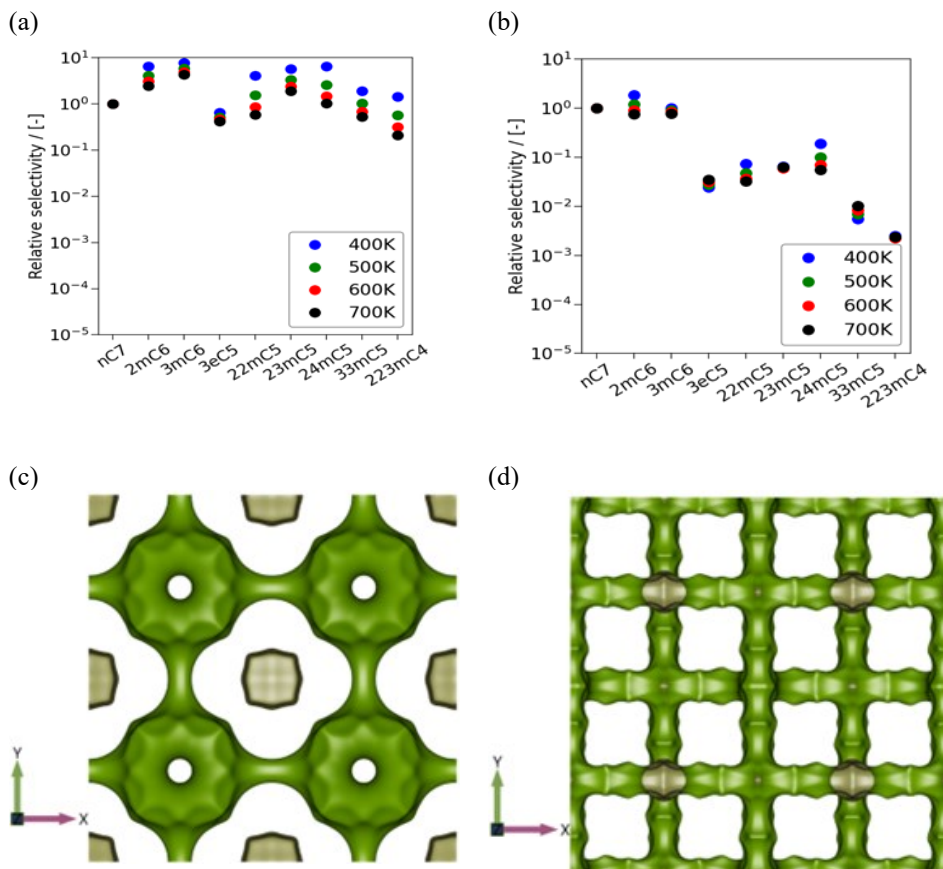
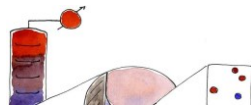


Fig 2. Selectivities of different heptane (C_7) isomers relative to n -heptane (nC_7) at reaction equilibrium in (a) ITQ-29-, and (b) MEL-type zeolites. The reactions are conducted at infinite dilution and the temperature ranges from 400 K to 700 K. Typical representations of (c) cage like pore structures in ITQ-29-type zeolite connected by narrow channels (4.1 4.1) and (d) straight channel like pore structures (5.3 5.4) in vertical and horizontal directions connected by intersections in MEL-type zeolite. The iRASPAsoftware⁵ is used to generate these images.



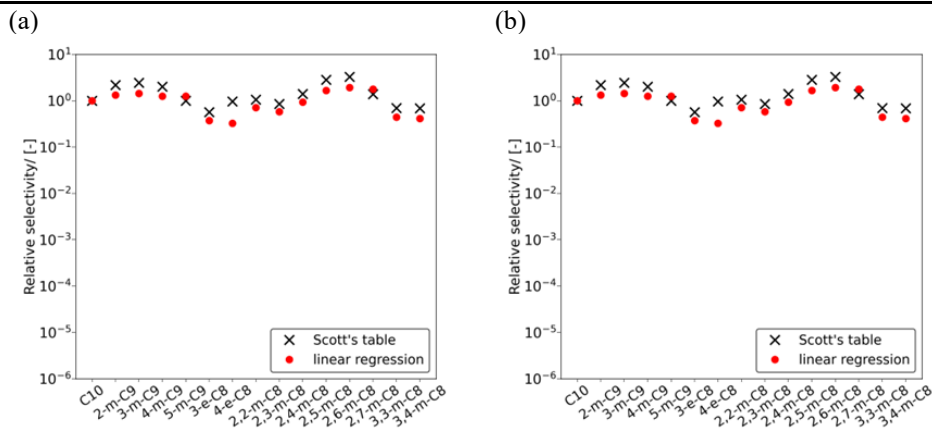


Fig. 3. Reaction equilibrium distribution of C_{10} isomers computed using the thermochemical properties obtained from Scott's tables⁴ and predicted by linear regression in (a) gas phase and (b) MTW-type zeolite at 500 K and infinite dilution.

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P2.24 Density, viscosity, heat capacity, gas solubility, and CO₂/hydrocarbon selectivity of ether-functionalized phosphonium-based ionic liquids

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Ionic liquids (ILs), which are salts that exist in the liquid state at room temperature, are typically composed of large asymmetric cations and organic or inorganic anions. Generally, the CO₂ solubility in ILs depends on the anion structure [1]. Ramdin et al. investigated the CH₄ solubility in ILs and found that interactions between nonpolar alkyl chains and CH₄ lead to increase CH₄ solubility [2]. They also found that the CO₂/CH₄ selectivity of ILs decreases with increasing IL molecular weight [2]. However, high CO₂ solubility in ILs often causes low CO₂/hydrocarbon selectivity; because ILs with high CO₂ solubility have void structures, many molecules can be physically absorbed, and therefore dissolve many hydrocarbons as well.

Makino et al. reported that the CO₂ solubility in ether- and ester-functionalized ammonium-based ILs was not significantly different from that in non-functionalized ILs [3]. However, the hydrocarbon solubility and CO₂/hydrocarbon selectivity of ether-functionalized ILs have not been investigated. Ramdin et al. reported the CH₄ solubility is higher in ILs containing large nonpolar alkyl-chains, which obviously interacts with the nonpolar CH₄ molecule [2]. We hypothesized that ether-functionalized ILs might decrease hydrocarbon solubility because of their relatively weak interaction with hydrocarbons. To prove this hypothesis, a correct would lead to improved



CO₂/hydrocarbon selectivity without reducing CO₂ solubility, based on the report by Makino et al.

In this study, we investigated the density, viscosity, heat capacity, CO₂ solubility, hydrocarbon solubility (CH₄, C₂H₆, C₂H₄, and C₃H₈), and CO₂/hydrocarbon selectivity of phosphonium-based ILs ([P₄₄₄₇][TFSA]: tributylheptyl phosphonium bis(trifluoromethanesulfonyl) amide ; [P₄₄₄₍₂₀₂₀₁₎][TFSA]: tributyl methoxyethoxyethylphosphonium bis(trifluoromethanesulfonyl) amide; and [P₄₄₄₍₂₀₁₎][TFSA]: tributyl(2-methoxyethyl)phosphonium bis(trifluoromethane sulfonyl)amide). The atmospheric density, and viscosity were measured at 273.15 – 363.15 K using the vibrating tube densimeter (Anton Paar, DMA5000M), and rotating-cylinder viscometer (Anton Paar, SVM 3000), respectively. The heat capacity was measured at 273.15 – 323.15 K using the micro differential scanning calorimeter (Setaram, microDSC VII evo). The high-pressure density was measured from 298.15 to 353.15 K up to 50 MPa using a vibrating tube densimeter (Anton Paar, DMA HP). The solubilities of CO₂ and hydrocarbons (CH₄, C₂H₆, C₂H₄, and C₃H₈) were measured at 313.15 K and 323.15 K up to 6 MPa using a magnetic suspension balance (Rubotherm) [4,5].

The CO₂ and CH₄ solubilities of [P₄₄₄₇][TFSA] are shown in Fig. 1. The solubilities of CO₂ and CH₄ showed the typical behavior of physical absorption and were negatively temperature dependent. We report on the atmospheric density, viscosity, heat capacity, high-pressure density, and thermodynamic evaluations of the gas dissolution of ether-functionalized and non-functionalized ILs, as well as CO₂/hydrocarbon selectivity evaluations in the presentation.

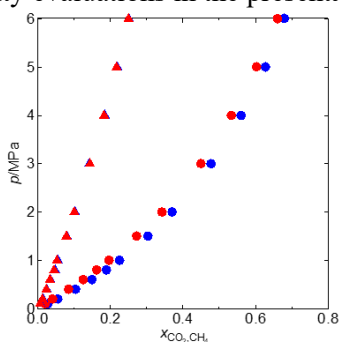


Fig. 1. Mole fraction-based CO₂ and CH₄ solubilities in [P₄₄₄₇][TFSA] at 313.15 K and 323.15 K. (Circle denotes CO₂ solubility. ●: 313.15 K, ●: 323.15 K, triangle denotes CH₄ solubility. ▲: 313.15 K, ▲: 323.15 K)



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P2.25 Techno-economic and Life-cycle Analysis of Methane Pyrolysis*P.B. Tamarona*, M. Ramdin, T.J.H. Vlugt*

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Methane pyrolysis (MP), also known as the thermal decomposition of methane, offers a promising route for producing CO_x-free hydrogen and advanced carbon from natural gas and biogas. Despite its potential, few studies have addressed the economic and environmental evaluation of MP [1-4]. This study aims to provide a comprehensive assessment of the entire MP supply chain at an industrial scale. We begin with a solid carbon market analysis to examine carbon quality requirements, price, market size, and applications. This analysis will form the basis for developing the MP process plant concept.

The concept will be designed further into a process plant model (flowsheet) in a process simulation software (Aspen Plus). This will include the necessary upstream and downstream separation processes. The reactor model will utilize thermodynamic and kinetic models validated with experimental data. Detailed thermal modelling of the reactor will be conducted, followed by an investigation on using different modes of supplying heat, such as electrical, microwave, and fuel combustion. Heat integration techniques will be implemented to minimize the plant's specific energy consumption. Additionally, the design of the upstream and downstream separation equipment for impurity removal, catalyst recovery, reactant recycling, and product upgrading, which are often overlooked in most conceptual MP process designs found in the literature [1-4], will also be discussed in detail.

A techno-economic analysis will be performed on the conceptual MP plant to estimate its capital and operating costs, net present value, payback time, and the levelized cost of hydrogen at varying carbon-selling prices. Additionally, a life-cycle analysis will assess the environmental impact, focusing on the CO₂ intensity of the entire MP supply chain, from the production of fossil- and bio-based methane to the various applications of hydrogen and co-produced solid carbon. We aim to identify scenarios that offer the lowest cost, lowest emissions, and an optimal balance between costs and emissions.



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P2.26 Melting vs freezing of hard spheres*Willem Gispen*, Marjolein Dijkstra*

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Melting and freezing are among the most common phase transitions on earth. In nature, the melting and freezing of water are critical in the environmental stability of our planet. In industry, crystalline materials ranging from metals to pharmaceutical drugs are processed with melting and freezing cycles to influence their properties. For decades, hard spheres have served as a fundamental model system to understand the freezing transition, leading to transferable insights into crystal nucleation and fluid structure. In contrast, the melting transition retains a multitude of open questions. The literature has primarily focused on the superheat limit, where melting is instantaneous, leaving a significant knowledge gap in the nucleation of melting.

We present a detailed study of the kinetics and thermodynamics of homogeneous hard sphere melting. We unveil significant asymmetries between melting and freezing of hard spheres, pertaining to the driving force and interfacial tension for nucleation. Furthermore, our results are a valuable test of classical nucleation theory that can be transferred to melting in atomic, molecular, and colloidal systems.

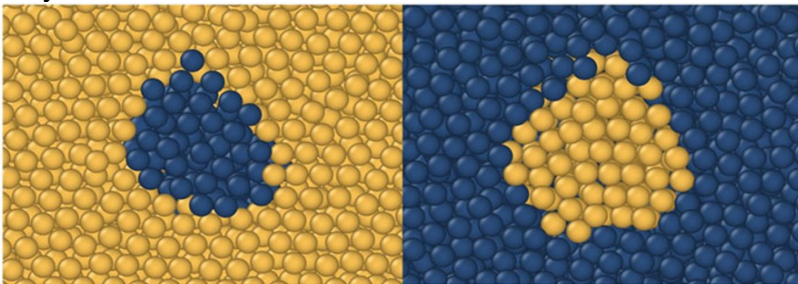


Fig.1. Nucleation during homogeneous melting (left) and freezing (right) of hard spheres.

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P2.27 High Temperature Thermochemical Heat Storage System for Industrial Heating Applications

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The industrial sector is responsible for 78 % of global carbon emissions, with 47 % attributed to the process heat (at various temperatures) and electricity. Fuel combustion provides almost 70 % of this energy, mainly for heating purposes, while the remaining 30 % is from electricity, mostly used for cooling and mechanical work. Therefore, decarbonizing industrial process heat is crucial for achieving net-zero CO₂ emissions. The integration of renewable electricity sources such as solar and wind, could support industrial decarbonization, provided a cost-effective and efficient storage solution is available to mitigate the intermittency of these sources and ensure the reliability of industrial heating systems. The present research focuses on thermal energy storage of surplus renewable electricity via a hybrid thermochemical/sensible heat storage utilizing porous media made of refractory redox metal oxides and electrically powered heating elements.

The proposed system will be developed and tested at a proof-of-concept scale. It consists of a well-insulated vessel filled with CaMnO₃ in a structured form (honeycomb or foam) as a reactive material. Energy is stored during the charging process by thermally reducing the reactive porous material (according to the redox reaction: $\text{MO}_x \leftrightarrow \text{MO}_{x-y} + \frac{y}{2} \text{O}_2$) and sensibly via electrical heating and industrial waste heat under atmospheric pressure. The stored energy is recovered by oxidation (discharging process) and sensible heating, achieved by passing ambient air through the porous, high-temperature reactive bed. Understanding the



hydrodynamics, heat/mass transfer, and chemical transport of the storage module is essential for the optimal reactor design and efficient operation. To achieve this, a numerical model to simulate the heat and mass transfer coupled with the chemical kinetics has been developed using ANSYS fluent. This model is employed to optimize the geometry of the storage module through a parametric study and to predict the storage performance at the laboratory scale. Additionally, it includes the numerical modelling of heat transfer within the multi-layer insulation to accurately predict heat loss through the storage walls.

This research is part of a recently funded project HERCULES through the EU-Horizon Europe program. The ultimate goal is to develop and test a first-of-its-kind prototype system that will demonstrate the applicability of the redox-based high-temperature storage system for industrial heating purposes.

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P2.28 Evaluation of the energetics of nitrogen adsorption on decorated iron oxides for the artificial photosynthesis of ammonia

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Ammonia is emerging as one of the most cost-effective solutions for hydrogen storage and transportation. However, its conventional production is both carbon and energy-intensive, accounting for approximately 2% of global carbon emissions and energy consumption. To address this issue, alternative synthetic routes, including photocatalysis, have been proposed. Photocatalysts for ammonia synthesis are typically carried out in metal oxides (such as titanium or iron oxides), and often enhanced with metallic nanoclusters to improve their efficiency [1].

This study investigates the energetics of nitrogen adsorption on different metallic nanoclusters using *in silico* methods. Specifically, an ONIOM approach using different levels of functional density models were employed to study the interactions of N₂ and NH_x ($x = 0$ to 3) with selected surfaces of these nanoclusters. The method, implemented in the Gaussian 16 package, was used for these calculations in combination with CPMD, used to pre-evaluate the energetics of the lattices using a lighter calculation method based on projector-augmented waves.

Preliminary results indicate that nitrogen adsorption energies on various metal surfaces are significantly lower, compared to a pure magnetite iron oxide (222), the core photocatalyst on which the metals are anchored. This suggests a higher affinity and potential for enhanced catalytic activity when these clusters are used. Notably, the adsorption of N₂ on Mo (110) and Fe (110) surfaces exhibited the lowest adsorption energies, at -0.21 eV and -0.15 eV, respectively. Conversely,



adsorption on Ru (110) showed a slightly positive adsorption energy ($E_{\text{ads}} = 0.02$ eV), making it the least favourable cluster studied.

These preliminary results show the potential of metallic doping in iron oxide nanoclusters for efficient N₂ adsorption, suggesting a route to design more sustainable and energy-efficient ammonia synthesis. Detailed analyses and complete results will be presented at the conference, providing a clearer picture of the catalysts for green ammonia production.

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P2.29 A novel apparatus for Vapor-Liquid Equilibrium measurements with in situ characterization of the liquid phase: Application in carbon capture

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The development of new industrial technologies for carbon (CO₂) capture and the improvement of current ones are the work of the coming decades. Amine-solvent based technology is one of the major carbon capture processes currently under development. This entails the use of amine mixtures in an aqueous solution, and depicting the mechanisms of the CO₂ absorption in the solvent is key to determine the distribution of the chemical species within the different phases at thermodynamics equilibrium. However, such an investigation remains relatively difficult, especially for the aqueous phase as the CO₂ absorption couples physical dissolution and several chemical reactions leading to formation of carbamate and bicarbonate-derived species. Thus, to achieve a better description of the concentration distribution of the different species that make up our chemical system, we developed a novel apparatus capable of both measuring VLE of CO₂/Amine-based solvents and monitoring over time the fate of the CO₂ within the liquid phase by Raman spectroscopy.

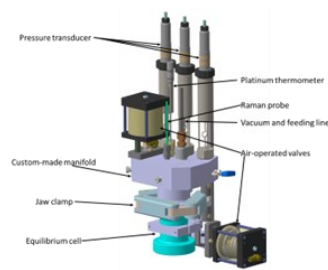
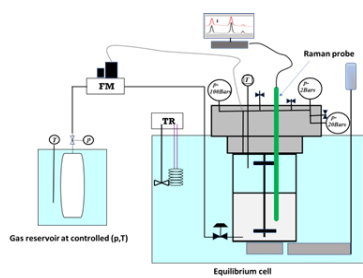


Fig. 1. Schematic diagram of the apparatus (left) and 3D view of the high-pressure cell with a detailed description of the apparatus will be given and the experimental method to measure VLE and monitor the kinetics of the CO₂ absorption will be presented. New data showing the Raman



signature of the generated species when CO₂ reacts with amines will be discussed and related to the nature of the amine.

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P2.30 Thermodynamic evaluation of the humic acid removal from aqueous solutions by using chitosan/activated carbon derivatives

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One of the main pollutants threatening the quality of water is natural organic matter (NOM) [1]. NOM is produced through metabolic reactions in water and it has been pointed out that it causes many problems, such as unpleasant taste and color of water, formation of disinfection by-products (DBP) and reduction of the amount of dissolved oxygen in water. Mainly, NOM are indicated as humic acid (HA) and fulvic acids (FA). Humic substance constitutes the highest percentage of NOM. Removal of HA substance from water is very important, because they have a harmful effect on the water quality human health. Many technologies have been examined for the removal of HA from water, including adsorption, membranes, advanced oxidation and photocatalytic oxidation. As the literature reveals, modified adsorbents, composite materials and nanomaterials have shown many satisfactory results for NOM removal from water [2].

Therefore, in this study, thermodynamic evaluation of the HA removal from aqueous solutions by using chitosan/activated carbon derivatives was performed. Chitosan (Cs), is a natural low-cost biopolymer exhibiting high adsorption capabilities due to the presence of amino and hydroxyl groups, [3] and activated carbon (AC) is one of the most common and effective adsorbents used in water treatment [4]. Several derivatives with different composition ratios, such as Cs/AC_1:1, Cs/AC_1:2 and Cs/AC_2:1, were examined in four different temperatures (293, 303, 313 and 323 K) in order to determine and evaluate the relative changes in free energy, enthalpy and entropy. The NOM was determined in this study by the UV-vis absorbance at 254 nm (UV₂₅₄). According to the results, was found that by increasing the temperature, there is a decrease in adsorption



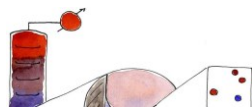
capacity of all applied ratios, indicating that the nature of adsorption is likely exothermic. ΔG^0 , ΔH^0 and ΔS^0 all found to have negative values. Thus, the thermodynamic parameters proved that adsorption of HA is a spontaneous exothermic process in which randomness decreases due to force of attraction between CS/AC and HA molecules. The adsorption data fitted well with the Langmuir isotherm model, whereas the adsorption kinetics followed better the pseudo-second-order model.

Acknowledgements

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P2.31 Insights into the Vapor-Liquid Equilibrium of mixtures containing 1-4 Dioxane/ Methanol/ Carbon dioxide

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Whatever the pathway the chemical industry will take to meet their greenness and sustainability goals over the next few years, an accepted fact appears: the development of new processes will require careful assessment of the solvent that should be used [1]. Polar organic compounds and their mixtures are widely used as solvent in a large variety of industrial processes [2], and there is a growing interest in developing more accurate models capable of describing/ predicting the phase equilibrium and related phase properties that take place in the process.

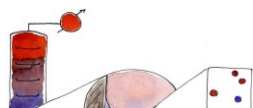
Chemical solvents are clearly most efficient by combining a chemical equilibrium with the physical dissolution process. Since water, a clean and very polar solvent, is used, the reaction is often promoted by electrolytic interactions, thus making the accurate description of the phenomena even more challenging. Thus, fluid-phase thermodynamic experiments are needed as they both allow achieving a better understanding of the interplays between molecules, and provide additional data- which are currently scarce [3] for model optimization and validation.

In this work, VLE of mixtures containing 1-4 Dioxane/ Methanol/ CO₂ are investigated. Phase composition was measured and the associated uncertainty was thoroughly evaluated, based on the characteristics for our apparatus. These two organic solvents are characterized by contrasted dielectric constants, yet much lower than that of water, and we have thereby considered the importance of this property on CO₂ dissolution. Future work will consider investigating increasingly complex mixtures by adding reactive species such as water together with an acid or a base. The resulting dataset will represent an important advance for model parametrization.



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P2.32 CO₂-based Electrothermal Energy and Geological Storage System – CEEGS

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The EU's long-term climate strategy and the European Green Deal highlight the pivotal role of renewable energies towards a clean energy system and decarbonisation. Despite technological progress and cost reductions, the stochastic nature and lack of dispatchability of wind and solar energy sources require fast development of large-scale energy storage to provide increased security of supply to the whole electrical system. The main challenge in integrating 100 % renewable energy sources (RES) into the energy system is the lack of large-scale energy storage to make intermittent renewable energy manageable. It is also imperative to diversify the portfolio of RES and combine the use of variable and dispatchable sources. This is the case, for instance, for deep geothermal systems in sedimentary basins, often considered uneconomic due to the large depths and relatively low (usually less than 100 °C) temperatures obtained. Furthermore, the IEA World Energy Outlook 2020 projections and the IPCC latest report stress that the Paris Climate Agreement ambition and the European targets cannot be reached without a substantial capture of CO₂ in hard-to-decarbonise sectors, such as cement, iron & steel and fertiliser production. So far, this effort has been seriously impaired by the high costs of CCUS technology, except where an economic value has been found for the captured CO₂. For energy storage, this economic value can be found in the CO₂ thermodynamic properties to act as a working fluid in energy storage systems and extract heat from geological formations.



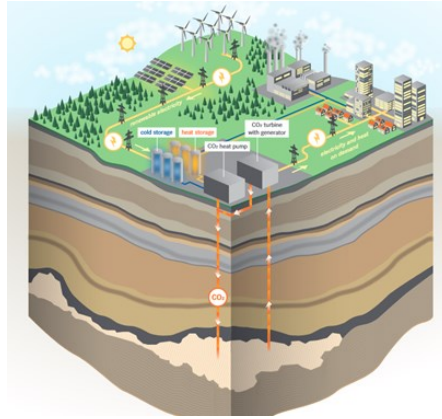


Fig. 1. CEEGS concept. Integration of surface/subsurface processes.

CEEGS (CO₂-based electrothermal energy and geological storage system) is a “high-risk/high-reward” concept aiming to bring a high-efficient, cost-effective and scalable energy storage technology by making feasible the integration of transcritical CO₂ cycles with underground energy storage achieved through the simultaneous CO₂ storage and geothermal heat extraction.

CEEGS has exceptional characteristics regarding: a) RES integration; b) scalable and up to large-scale energy storage; c) combined CO₂ geological sequestration; d) capacity for integration with large CO₂ producers; e) heating and cooling integration; f) low environmental impact and costs.

The concept is based on a hybrid system for energy storage and underground carbon utilisation in a closed-loop as heat transfer fluid (see Figure 1). If successful, it would allow high energy storage capacity due to underground repository and partial CO₂ sequestration in the terrain. It utilises the synergies of transcritical systems and underground storage with high energy capacities compared to only surface tanks and additional contributions of thermosiphon and geothermal heat. It implies low costs and environmental impact. It is a trigeneration system that can provide electricity, heat and cold. The key challenges for advancing this concept are related to the interface between the transcritical cycle and the subsurface storage.